2022 IEEE 12th International Conference “Nanomaterials: Applications & Properties” (IEEE NAP-2022)

ABSTRACTS

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2022 IEEE 12th International Conference “Nanomaterials: Applications & Properties” (IEEE NAP-2022)

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**Kraków** also spelled Cracow, is the city and capital of Małopolskie województwo (province), southern Poland, lying on both sides of the upper Vistula River. One of the largest cities in Poland (~1.4 million inhabitants if you include the surrounding communities), it is known primarily for its grand historic architecture and cultural leadership; UNESCO designated its old town area a World Heritage site in 1978. Its marketplace, Rynek Główny (Main Square), has existed since the 13th century, and a modern landscaped area is laid out on the site of past fortifications.

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The [NANONET](#) Foundation was established as a source of reliable information allowing to discover and experience the nano-world. Created by volunteers, it aims at promoting the development of entrepreneurship based on new technologies and, furthermore, at popularising the results of research and development works conducted in the field of nanotechnology. The Nanonet Foundation, established in 2006, includes scientists, young researchers, Ph.D. and undergraduate students, business leaders, research organizations from the public and private sectors, and many other professionals with various backgrounds.

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TRACK 1

“NANOMATERIALS SYNTHESIS & SELF-ASSEMBLY”
Electrical Interface Between Carbon Nanotubes & Metallic Electrodes for Industrial Applications

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Carbon Nano Tubes (CNTs) have shown unrival properties combining both excellent electrical conduction as well as thermal and mechanical properties [1, 2]. In this study particular attention are payed in the electrical conductivity and its possible application in industry. The aim of this work is to increase electrical conductance of industrial Al wires by introducing CNTs in the bulk of the wire, in the goal to lightening Al cables.

In order to achieve the increasing of Al wires conductivity, it is important to determine the conditions to obtain the best conductance in a metal/CNT interface. Several devices were prepared using both Single Wall CNT (SWCNT) grown in laboratories and commercial samples bought from different companies. Interface contacts were realized using different metals. The characterization of each sample consisted on resistance measurements and electron microscopy (TEM, SEM and EDX) in order to investigate their structure. Measurements on a large and statistically meaningful sample of metallized CNTs devices were performed. The study shows that the best candidates for a good electrical interface are SWCNT, with Pd electrodes, which is in good agreement with previous reported work [2, 3]. It is also showed that Ti electrodes, after annealing [4] can be an interesting compromise in an industrial application, and an industrial method to include SWCNT in Al cables, with an hybrid interface was tested. The study also shows the importance of CNTs purity for good electrical conductivity, in particular for commercial samples.

REFERENCES

Effect of Rapid Thermal Annealing on the Optical Properties of InAs Quantum Dots Grown on (100) and (311)B GaAs Substrates by Molecular Beam Epitaxy

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Abstract ID #NSS-0023

The effect of Rapid Thermal Annealing (RTA) on the optical properties of InAs Quantum Dots (QDs) grown at an As overpressure of 2x10⁻⁶ Torr by Molecular Beam Epitaxy (MBE) on (100) and (311)B GaAs substrates was investigated using Photoluminescence (PL) technique. PL results showed that for the as-grown samples, the QDs grown on the high index plane (311)B have lower PL intensity and lower Full Width at Half Maximum (FWHM) than those grown on the conventional (100) plane. The latter demonstrates that the (311)B QDs have better size uniformity than (100) QDs [1]. Compared with as-grown samples, a blue-shift was observed for all samples with increasing annealing temperature from 600 °C to 700 °C. For (100) samples a narrowing of the FWHM was observed with increasing annealing temperature from 600 °C to 700 °C. However, in (311)B samples the FWHM showed a different behaviour: it slightly increased when the samples were annealed at 600 °C and then decreased when the annealing temperature increased to 700 °C. As expected, the PL peak intensity for all samples increased when the laser excitation power increased. The PL peak energy temperature dependence showed a strong redshift when the temperature was increased from 10 K to 120 K. The PL peak energy exhibited an abnormal S-shape behaviour as function of temperature for all samples. Most samples exhibited a significant enhancement in their activation energies when annealed at 600 °C and 700 °C, suggesting that annealing annihilated defects created during sample growth.

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REFERENCES

Stability of InP/ZnSe/ZnS Quantum Dots with Thick or Thin ZnS Shell, and their Lifetimes in Light-Emitting Diodes: Relation of Shell Thickness and Surface Chemistry

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Abstract ID #NSS-0032

In typical III–V colloidal InP Quantum Dots (QDs), an inorganic ZnS outermost shell is used to provide chemical stability when overcoated onto InP core.[1] However, we found a faster degradation of quantum efficiency in the case of InP/ZnSe/ZnS QDs with a thicker ZnS shell than that with a thin ZnS shell when 1-octanethiol was applied as a sulfur source to form ZnS outmost shell. Herein, we demonstrate that 1-octanethiol induces the form of weakly-bound carboxylate ligand via proton transfer on the QD surface, resulting in a faster degradation at UV light even though a thicker ZnS shell was formed onto InP/ZnSe QDs. Detailed insight into surface chemistry was obtained from proton nuclear magnetic resonance spectroscopy and thermogravimetric analysis–mass spectrometry. However, the electroluminescence devices of InP/ZnSe/ZnS QDs with thick or thin ZnS shells show surprisingly the opposite result to the stability of QDs, where the operating lifetime of QDs with thick ZnS shell is longer than that with thin ZnS shell. In general, QDs can be degraded by oxidation, decomposition, hydration, and UV exposure, by which the lifetimes of QD devices are mostly known as following a trend of photo-, chemical, and thermal stability of QDs.[2] In this study, we discuss the mechanism of the stability of QDs and QD light-emitting diodes based on our results and elucidate why the stability of QDs is different from the lifetime of devices. As a result, We believe this better understanding of the relation between QDs and QD devices paves the way to industrially feasible QD light-emitting diodes.

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The Influence of Cu on the Manufacturing and Catalytic Activity of Nanoporous Gold

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Abstract ID #NSS-0034

Nanoporous gold (npAu) can be synthesized using different gold alloys, typically containing Ag as the second metal. By removal of the sacrificial second metal by corrosion, a nanoporous Au sponge is formed, with ligaments and pores on the order of 30 to 50 nm [1, 2]. Yet, during synthesis, not all of this second metal is removed and fractions below 1 at% typically remain. For other second metals, Cu is expected to change the catalytic properties significantly [3]. The aim of the project is to study Cu as sacrificial second metal.

Synthesis of npAu-Cu from AuCu alloy is a complex procedure, mostly because of the passivated surface and inhibited corrosion phenomena observed in those materials [4, 5]. To improve our understanding of the leaching of Cu, a series of experiments were performed to study the corrosion process. Here we compare different corrosion methods, beginning from free corrosion (as a standard synthetic route for AuAg) finishing with an optimized potentiostatic dealloying procedure. The catalytic properties of npAu-Cu were studied.

Results show that the activity of the npAu-Cu material is a strong function of the amount of Cu remaining after corrosion, in particular at the catalyst's surface, investigated by X-ray Photoelectron Spectroscopy (XPS). By a careful choice of synthetic parameters during the preparation of the alloy and its corrosion, the overall content of Cu could be decreased below 5 at% within the bulk, yet surface concentrations between 25 at% and 5 at% were detected. Indeed, the atmospheric parameters during catalysis, for example the presence of O₂ was determined to alter the chemical state of the Cu on the surface and even increase its concentration at the surface. The most active samples contained only 5 at% of Cu at the surface, corresponding to a dilute alloy of Cu within the Au matrix. In order to distinguish between chemical and structural changes, such as a varying surface area because of different ligament sizes, the surface area was determined electrochemically and through Scanning Electron Microscopy (SEM) analysis. The data reveal an obvious influence in key synthetic steps at the master alloy synthesis, as well as the dealloying procedure.

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REFERENCES

The Versatile Synthesis of Polyhedron Core-Shell \( \text{Cd}_{0.1}\text{Zn}_{0.9}\text{Se}/\text{Cd}_{x}\text{Zn}_{1-x}\text{S}/\text{ZnS} \) Quantum Dots

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Abstract ID #NSS- 0041

One of the most effective strategies for reducing the surface defects in nanocrystals is the shell growth on the already formed cores. This approach not only increases the Photoluminescence Quantum Yield (PL QY) but also prevents the diffusion of cations and anions from the core material. Gram scale synthesis of the green-emitting core \((10 \text{ g})\) was performed by interaction of highly reactive substituted selenourea \((\text{Z})-\text{N}(\text{octadec-9-enyl})\text{morpholine-4-carboselenoamide})\) with the cadmium and zinc linoleates mixture at 240 °C. Verification of the shell growth method based on the volume ratios of the core and the core with a shell led to the creation of a series of core/shell/shell \(\text{Cd}_{0.1}\text{Zn}_{0.9}\text{Se}/\text{Cd}_{x}\text{Zn}_{1-x}\text{S}/\text{ZnS} (x = 0.1; 0.25; 0.4; 0.6; 0.75)\) Quantum Dots (QDs). Deposition of the first shell \((\text{Z})-1-(\text{octadec-9-enyl})-3\text{-phenylthiourea})\) of \(\text{Cd}_{x}\text{Zn}_{1-x}\text{S}\) composition with a thickness of 2 monolayers (MLs) (epitaxial growth) resulted in blue \((x = 0.1\) and 0.25\) and red \((x = 0.4; 0.6\) and 0.75\) shifts in emission bands and an increase in PL QY (up to 71 %). The deposition of the second ZnS shell (2 MLs), the same for all compositions, was not epitaxial to the core, which brought a change in shape but did not affect the optical properties of the material. The analysis of \(\text{Cd}_{0.1}\text{Zn}_{0.9}\text{Se}/\text{Cd}_{x}\text{Zn}_{1-x}\text{S}/\text{ZnS}\) core/shell/shell by EDS, XPS and XRD methods, confirmed the accordance of the initial ratios with the given compositions and sizes.

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Visible-light Photocatalytic Performance of the State-of-the-Art Al: SrTiO$_3$@δ-FeOOH Hierarchical Core@Shell Nanoheterostructures

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Abstract ID # NSS- 0044

Perovskites (ABO$_3$) with suitable band gap and superior properties are promising materials for photocatalytic applications like photocatalytic degradation of organic dyes or antibiotics which are encountered in wastewater or water splitting [1, 2]. Strontium titanate (SrTiO$_3$) has an excellent photocatalytic performance but only in the presence of UV light due to the high value of their band gap (3.2 eV). In order to enhance the photocatalytic activity of this material under visible light, SrTiO$_3$ nanoparticles were surface decorated with double co-catalyst system consisting of Al$_2$O$_3$ [2] and iron oxyhydroxide (FeOOH). Thus, the targeted multifunctional nano-heterostructured composites was developed considering different polymorphic forms of the FeOOH oxyhydroxide. Strontium titanate nanoparticles were prepared by ceramic method using stoichiometric amounts of strontium carbonate (SrCO$_3$), titanium dioxide (TiO$_2$) and aluminum oxide (Al$_2$O$_3$) which were grinding in presence of ethanol and furthermore annealed at 1000 °C for 10 hours. The deposition of iron oxyhydroxide on the surface of perovskite particles was achieved by precipitation of Fe$^{3+}$ ions under various experimental conditions. The obtained materials (Al: SrTiO$_3$@β-,γ-,δ-FeOOH) were characterized in terms of structure and optical properties. Their visible-light photocatalytic activity was also evaluated by performing degradation tests over Tropaeolin 00 dye (Orange II). The best photocatalytic performance was achieved for the Al: SrTiO$_3$@δ-FeOOH material which was able to decompose 97% of dye in 45 minutes.

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Synthesis Through Wet Chemical Route and Structural Behaviour of Cerium Doped Copper Ferrites

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Abstract ID #NSS-0045

Spinel ferrites are currently used for a wide area of applications due to their structural, magnetic and electric properties. Over the years a large number of methods were developed and improved in order to obtain simple or mixed ferrites with rare earth metal cations [1]. Among them is included the co-precipitation synthesis pathway that uses simultaneous precipitation of metal salts. During the synthesis process, the mixture presents some transitionary stages from hydroxides to oxide-hydroxides and finally to the most stable form, the mixed oxides – $AB_2O_4$.

Rare earth ferrite such as Ce doped Cu ferrites prefers a cubic crystallization system with $Ce^{3+}$ occupying the octahedral sites due to the ionic radius. The insertion of $Ce^{3+}$ may cause structural modification over the structure of the ferrite as some studies report that substituted Cu ferrite have a dual crystallization structure, one with $Fd-3m$ symmetric group specific to cubic structure and other with $I41/amd$ space group specific to tetragonal structure [2]. This structural change may be caused by cation substitution and heating treatment of the Cu ferrites. Also, the exchange of electrons that occurs in the ferrite structure between the Fe-Fe, Fe-Cu, Fe-Ce and Cu-Ce cations produces changes in the properties of the nanostructures. It has been shown that high temperature heat treatments of $CuFe_2-xCe_xO_4$ ferrites produce significant structural modifications and influence the properties of the nano-structures [3]. The irreversible structural transition favours a segregation process that forms copper and cerium oxides simultaneous with oxidation of $Ce^{3+}$ to $Ce^{4+}$.

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The Effect of the Growth Rate on the Optical Properties of Self-assembled InAs Quantum Dots Grown by Molecular Beam Epitaxy on GaAs (100) Substrates

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The fabrication of self-assembled InAs quantum dots grown on GaAs substrates have attracted much attention both for basic physics and optoelectronic device applications [1]. The structural and optical properties strongly depend on growth conditions, such as growth temperature, growth rate and the capping layer material. Growth studies have also been carried out with the intention of controlling size, shape and density of the Quantum Dots (QDs) [2]. In this work, we have investigated the effect of growth rates on the optical properties of Indium Arsenide (InAs) QDs grown by Molecular Beam Epitaxy (MBE) on semi-insulating (100) GaAs substrates using Photoluminescence (PL) technique. For this purpose, four types of InAs QDs grown under similar conditions but with different growth rates in terms of Monolayer/s (ML/s), namely, 0.011 ML/s, 0.022 ML/s, 0.033 ML/s and 0.066 ML/s. The PL emission was studied as a function of laser power at 10K. One PL peak was detected in the PL spectra of all QDs samples. However, the PL peak energy was dependent on the growth rate. The PL peak energy of the InAs QDs grown at 0.011 ML/s, 0.022 ML/s, 0.033 ML/s and 0.066 ML/s was 1.27 eV, 1.26 eV, 1.25 eV and 1.24 eV, respectively. Increasing the growth rate from 0.011 MLs-1 to 0.066 MLs-1 led to a red shift of emission energy by approximately 10 meV for all QDs samples investigated. Furthermore, as the growth rate increased from 0.011 to 0.066 ML/s, an enhancement of the PL intensity and a decrease of the PL FWHM (Full-Width at Half Maximum) were observed. The significant decrease of the PL FWHM provided evidence that the uniformity of the QDs increased [3]. Temperature-dependent PL study was carried out in the 10 K – 140 K temperature range. For all QDs samples there was a strong redshift with increased temperature range.

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REFERENCES

Efforts in Searching for an Efficient Photocatalyst – a New Synthesis Path of Potassium Vanadate with Controllable Microstructure and Morphology

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Abstract ID #NSS- 0058

Water quality is one of the primary challenges that societies will face during the 21st century. According to UNESCO-IHP International Initiative on Water Quality, the availability of the world’s water resources is increasingly limited due to the worsening pollution of freshwater. From the known methods of treating wastewaters, photocatalysis is a promising technology to solve environmental problems. Therefore, new and efficient photocatalysts that will be active in visible light and/or near-ultraviolet light, biologically neutral, photostable, and resistant to the influence of the environment are constantly being sought. Recent studies demonstrate that vanadium compounds with transition metals from block d or metals from block p (e.g. Ag₂VO₄ [1] and BiVO₄ [2]) exhibit promising visible-light photocatalytic activity. The conducted research is focused on nanostructured vanadates because shape and size, as well as specific surface area, play a significant role in photocatalytic properties. On the other hand, the microstructure of the material also strongly influences its photocatalytic activity. Vanadates occur in many forms, most with a single vanadium valence state of 5+. However, the chemical valence state of vanadium can vary, depending, e.g., on the synthesis method.

The potassium vanadates are so far the least tested part of the vanadates as a photocatalyst. Thus in our research, we focused on searching for a new synthesis method that allows control of the microstructure and morphology of these compounds. We developed the novel, one-step method - the Liquid-Phase Exfoliation with Ion Exchange (LPE-IonEx). The LPE-IonEx method is characterized by a one-step synthesis route, wherein the reaction occurs spontaneously at room temperature (RT). The main advantage of this method is the possibility of control of the product morphology, microstructure, the ratio V⁴⁺/V⁵⁺ on the sample surface, and the bandgap energy width by varying reaction conditions [3].

In this study, the hydrated and non-hydrated phases of potassium vanadate were synthesized and investigated as photocatalysts. By changing the synthesis parameters, different compositions, morphology, width of bandgap energy, and V⁴⁺/V⁵⁺ ratio were obtained. Potassium vanadates’ structural, morphological, and optical properties were characterized using different techniques such as XRD, FTIR, XPS, PXMS, TGA with MS, Ν₂ adsorption, SEM, PL, and UV-Vis DRS. Their photocatalytic activity was evaluated by the degradation of organic dye under simulated solar light illumination. Our results have shown that potassium vanadates synthesized by the LPE-IonEx method absorb a significant part of the light spectrum in the visible range and degrade over 90% of organic dye at a time below 30 minutes. Observed excellent photocatalytic performances resulting from the specific structural properties, which were provided by the proposed innovative LPE-IonEx method.

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REFERENCES

The Thermal Mode Crucial Influence on the ZnSeS QDs Formation

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Abstract ID #NSS- 0060

The qualitative and quantitative diversity of existing methods for the synthesis of chalcogenide nanomaterials is constantly being updated. Attempts to improve an already functioning synthesis scheme may lead to the emergence of a new promising directions. It turned out that the ability of substituted thio- and selenoureas to form stable complexes with metal carboxylates can allow one-pot and hot-injection methods to be combined in the ZnSeS quantum dots (QDs) synthesis. After the formation of zinc linoleate complexes with various substituted thio- and selenoureas in a single reaction system at relatively low temperatures (80 °C), we introduced them into a medium heated to the desired temperature. The complexes decomposing at different rates led to the formation of ZnSeS QDs of various shapes and sizes. Despite these differences, the nanocrystals grew in the same cubic phase at different nucleation and growth temperatures. It was demonstrated that even ZnSe0.1S0.9 and ZnSe0.3S0.7 QDs prepared at such low, for the growth of chalcogenide semiconductors, temperatures (160 °C and 180 °C) have a narrow size distribution and a good Photoluminescence Quantum Yield (PL QY up to 24 %). In general, the optical characteristics of the synthesized nanomaterials enable further development of this synthesis method and transfer of it to other compositions.

ACKNOWLEDGMENTS

Authors appreciate the financial support from the project “High-sensitive and low-density materials based on polymeric nanocomposites” - NANOMAT (No. CZ.02.1.01/0.0/0.0/17_048/0007376) and grant LM2018103 from the Ministry of Education, Youth and Sports of the Czech Republic.
Synthesis and Characterization of Graphene Oxide from Residual Biomass

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Abstract ID #NSS-0062

Graphene oxide (GO) is a member of the graphene family that is intensively used in many fields such as electronics, environmental protection, and biomedical applications. GO is mainly produced from commercially available graphite powder. In this study, however, GO was synthesized from alternative carbon-rich biomass residues that are readily available: spent tea leaves, and coffee waste. These residues were treated with dilute HCl to remove impurities and then soaked in NaOH to activate their carbon. Highly porous GO nanomaterials were successfully synthesized using the modified Hummer’s method after pyrolysis of the biomasses at a moderate temperature. These nanomaterials were characterized using FTIR, Raman spectroscopy, SEM, and XRD. FTIR results indicated the removal of oxygen (C-O and O-H bonds), carboxyl, carbonyl, carboxylic, and epoxy functional groups from the biomass through pyrolysis. Raman spectroscopy of the GO particles revealed the extent of the oxidation process. SEM images showed vascular-shaped graphene layers with porous and semi-porous surfaces. X-ray diffraction patterns showed an amorphous shape. The properties of the synthesized GO particles were compared with GO produced from the conventional source: graphite. The results indicated considerable similarities. Hence, biomass residuals can be considered a viable, environmentally-friendly source for GO.

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STM Study of Stereospecific on-Surface Cyclodehydrogenation and Planarization of Bispentahelicenes on Au(111) Surface

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Abstract ID #NSS-0063

The subject of our research is chiral crystallization of carbohelicenes into homochiral structures. 2D chiral crystallization of carbohelicenes on metal surfaces is of paramount importance for light sensors or for electron-spin filters. Here, we report the 2D chiral crystallization of 2,2'-bispentahelicene on Au(111) and its thermal-induced dehydrogenation studied with Scanning Tunneling Microscopy (STM). The low coverage deposition of bis[5]helicenes on Au(111) kept at 400 K, leads to formation of heterochiral zigzag chains of the (M,M)- and (P,P)-enantiomers growing along the herringbone reconstruction pattern. In the closed-packed monolayer, both enantiomers self-assemble into racemic phase and rotational and mirror domains can be differentiated. Due to its strong sterical overcrowding in its adsorbate state, the (P,M)-meso form was not observed on the surface.

Upon annealing the substrate to approximately 670 K and subsequent cooling to 50 K, the characteristic twisted shape of the bis[5]helicenes with protrusions is no longer observed and two-dimensional homochiral domains of planar coronocoronene molecular species can be distinguished. The transformation from helical to planar chiral molecules via dehydrogenation and loss of eight hydrogen atomes was confirmed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Further STM measurements at 7 K affirmed the formation of mirror and rotational 2D homochiral conglomerate domains of Sp- and Rp-coronocoronene.
Effect of the Synthetic Route on the Defect Structure and Redox Activity of TiO$_{2-x}$ Nanocrystals

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Abstract ID #NSS-0065

Nano-sized titanium oxide are well-known due to their excellent photocatalytic properties. However, some researchers have reported on the antioxidant properties of TiO$_2$ surfaces and nanocrystals associated with a structure of oxygen-deficient TiO$_{2-x}$ [1]. High amount of oxygen vacancies stabilized by Ti$^{3+}$ or Ti$^{2+}$ ions is supposed to be responsible for the redox properties of TiO$_{2-x}$ Nanoparticles (NPs).

To evaluate the correlation between the defect structure of TiO$_{2-x}$ NPs and their antioxidant behavior, the original method for TiO$_{2-x}$ NPs synthesis based on hydrolysis of titanium butoxide followed by a peptization process has been proposed. Changing the amount of nitric acid as a catalyst and peptizing agent, two types of TiO$_{2-x}$ NPs (Ti-NPs#1 and Ti-NPs#2) of the same size about 5 nm, but different Ti$^{3+}$(Ti$^{2+}$)/Ti$^{4+}$ ratio have been obtained in the form of water colloid solutions. The structure and properties of the obtained Ti-NPs#1 and Ti-NPs#2 samples have been analyzed by TEM, XRD, XPS and optical spectroscopy methods. Electron donating properties and ROS scavenging activity of both types of titania NPs against hydroxyl radicals ($\cdot$OH) formed during X-ray irradiation of water solutions have been studied.

The mechanisms of redox activity and role of the peptizing agent in obtaining defect structure of TiO$_{2-x}$ NPs are discussed.

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REFERENCES

Optimization of Ligand Concentration on the Optical Properties of Colloidal MoS$_2$ Quantum Dots

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Abstract ID #NSS-0081

In this work, we report an investigation of the concentration of ligands on blue light-emitting MoS$_2$ quantum dots (QDs), which is a highly studied material of transition metal dichalcogenides (TMDC) class. The optical and electronic properties of TMDC nanomaterials are highly influenced by the surface-bound ligands due to edge effects. Optimization of the concentration of ligands and their effect on the optical properties of MoS$_2$ QDs are studied. Highly luminescent, narrow size distribution, blue-emitting MoS$_2$ QDs are synthesized, which find applications in fabricating blue LEDs, lasers, and UV photodetectors.

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Hybrid VIS and NIR Emission of (6,5) SWCNTs Modified with Fluorescein Through Aryl Diazonium Salt Chemistry

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Abstract ID #NSS- 0082

Recently, the fluorescence of Single-Walled Carbon Nanotubes (SWCNTs) in the 2\textsuperscript{nd} Near-Infrared Window (NIR-II) between 900 – 1700 nm opened an opportunity for imaging of living systems with a greatly improved imaging resolution, deep tissue penetration of NIR photons, low autofluorescence, and reduced light scattering in living tissue [1]. On the other hand, the lack of visible fluorescence somewhat restricts the potential of biological studies as the material can be visualized only by not-so-common InGaAs detectors. Not only dual VIS-NIR fluorescence could expand the range of spectrometers that can visualize SWCNTs in living systems, but it also opens new exciting possibilities for SWCNTs applications. We hypothesized that one of the potential ways to introduce the VIS emission, while achieving the enhanced NIR emission of SWCNTs can be realized with the use of well-known fluorophores and aryl diazonium salt chemistry [2]. Fluorescein, among other organic fluorophores, appeared to be a promising candidate for our purpose [3]. Not only, its emission and absorption properties are complementary to those of (6,5) SWCNTs used in our study minimizing the inner filter effect induced by SWCNTs, but also we were able to synthesize 5-fluoresceindiazonium tetrafluoroborate (5-FN2) as a stable solid.

In this report, 5-FN2 was used to create local sp\(^3\) defects on (6,5) SWCNTs dispersed in 0.2% SDS aqueous solution. Due to the dissociation of 5-FN2 in the water, we studied the effect of pH on the grafting process on (6,5) SWCNTs establishing that the reaction is most effective at pH 5. So obtained F-(6,5) SWCNTs were further purified by dialysis with a simultaneous exchange of surfactant for non-ionic Pluronic F 127. F-(6,5) SWCNTs conjugates showed hybrid light emission properties: relatively high fluorescein emission in VIS range with fluorescence quantum yield of 8.9% at pH 6.5 and enhanced, red-shifted NIR emission from E11* energy level due to the incorporation of local sp3 defects. F-(6,5) SWCNTs exhibit both VIS and NIR emission in pH range from 1 to 12 with optical properties directly reflecting the fluorescein chemical structures in water at given pH.

Our study shows that 5-FN2 appears as a useful, readily available reagent for modification of optical properties of SWCNTs in NIR-II with the benefit of adding visible fluorescence. The approach can be useful, particularly for biomedical applications where dual-channel Vis and NIR imaging could be performed. In addition, the pH sensitivity of the F-(6,5) SWCNTs gives room for using ionic interactions as an anchor e.g. in developing pH-driven drug release nanoplatforms.

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Conference Track: “Nanomaterials Synthesis & Self-assembly” 01nssa-15
Self-assembled Monolayers on Aluminium – Optimization of Structure and Stability

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Abstract ID #NSS- 0092

Aluminium is a versatile, yet inexpensive metal that is nowadays commonly used in various industrial applications. It is a key material not only for components of macroscopic objects such as aircrafts or vehicles, but also for electronics, where it customarily acts as the gate of the transistor. Such wide utilization of aluminium naturally drives the interest in functionalizing the aluminium surface to further enhance its potential, especially in the field of hydrophobic coatings [1, 2]. One of the possibilities to tune the properties of the aluminium surface are Self-Assembled Monolayers (SAMs). However, archetypal thiol-based systems, which have been robustly studied on the gold surface, do not apply to the oxidized aluminium surface. An alternative for thiols might be provided by carboxylic and phosphonic acids that can form with this substrate bidentate and tridentate bonds, respectively.

In our work, we have optimised the process of forming hydrophobic coatings on the aluminium surface employing SAMs based on aliphatic carboxylic and phosphonic acids. We considered the three crucial factors that affect the properties of the final monolayer: solvent, incubation time, and incubation temperature. Spectroscopic methods (IRRAS, XPS) and wettability measurements (static contact angle) were used to determine the most favourable incubation conditions in terms of the monolayer structure. Subsequently, we compared the hydrolytic and thermal stability of the selected carboxylic and phosphonic systems.

Such a systematic study enabled us to determine optimal conditions for SAMs formation on the aluminium surface.

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REFERENCES


N-heterocyclic Carbenes – the Design Concept for Densely Packed and Thermally Ultra-stable Aromatic Self-assembled Monolayers

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Abstract ID #NSS-0095

Self-Assembled Monolayers (SAMs) provide a versatile tool for surface and interface engineering and are commonly used for numerous applications in molecular/organic electronics. Currently, most of SAMs applications involving metal substrates rely on using thiolates. Recently, however, a new direction was proposed that exploits N-Heterocyclic Carbenes (NHCs) [1, 2]. This development is based mainly on studies indicating significantly higher thermal and chemical stability of NHC SAMs compared to thiolates. The NHC SAMs are usually formed using an imidazolium moiety, which links NHC molecules with the metal substrate through a carbene C atom. Experiments and calculations indicate that vertically oriented NHC SAMs – which are useful for surface modification – can only be formed using bulky side groups (e.g. isopropyl) attached to nitrogen heteroatoms in imidazolium moiety [3]. However, this commonly accepted design concept results in at least three times lower surface density of NHC SAMs compared to thiols [3], noticeably diminishing the chemical and physical impact of the functionalization and therefore hindering the potential of NHC SAMs for surface and interface engineering. Following our recent successful example of densely packed NHC SAMs formation [4], in the current work [5] we conducted a systematic experimental analysis (XPS, HRXPS, NEXAFS, SIMS, TP-SIMS, WCA) for a series of such monolayers demonstrating that, contrary to commonly accepted model, NHC SAMs with short side groups can form vertically oriented densely packed monolayers exhibiting a doubled surface density compared to the NHC SAMs reported before. Moreover, the thermal stability for such optimized monolayers is ca. 160 K higher (~0.5 eV increase in desorption energy) compared to NHC monolayers considered currently [3] as a model system. Altogether, the obtained results provide a well-defined concept of molecular design and the preparation procedure, paving the way to the fabrication of densely packed and thermally ultra-stable functional aromatic SAMs on the NHC basis. Such SAMs can be particularly useful for applications in organic and molecular electronics, where the high thermal stability of functional monolayers becomes frequently critical considering (i) thermal processing steps during the assembly of a particular device and (ii) overheating problems related to a poor heat transport at the molecule-metal interface. The solution-based preparation procedure suggested by our study simplifies the assembly of devices, making the use of NHC SAMs attractive also in this regard.

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Conference Track: “Nanomaterials Synthesis & Self-assembly” 01nssa-17

WC-based Cemented Carbides with Nanostructured NiFeCrWMo High-Entropy Alloy Binder

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Abstract ID #NSS- 0102

Due to high hardness, strength, and wear resistance, WC-based cemented carbides with Co binder are widely used in various industries [1, 2]. However, the industry development leads to an increase in the requirements for materials, which prompts researchers to search for ways to improve the properties of cemented carbides [2-4]. Thus, today there are two directions for enhancing the properties of cemented carbides: 1) the use of the new sintering methods (spark plasma sintering, Electron-Beam Sintering (EBS)), which allows for preserving the original particle size of the cemented carbides [2]; the use of alternative materials (nickel, chromium-based alloys, High Entropy Alloys (HEA)) as a binder to replace cobalt [3]. Thus, the use of nanostructured HEAs may significantly improve the properties of cemented carbides [4]. This work aims to obtain WC-based cemented carbides with nanostructured HEA binder by EBS. Commercial WC powder (90 wt. %) with a particle size of 4-6 μm and nanostructured FeCrNiWMo HEA (10 wt. %) obtained by mechanical alloying (10 h, 400 rpm, petrol) were chosen as starting materials. Mixing was carried out in a planetary ball mill (1 h, 200 rpm, alcohol), and EBS was carried out on the ELA-6 machine at 1250 °C, 1350 °C, and 1450 °C for 4 min, and for 10 s and 2 min at 1450 °C. Sintered samples were investigated by XRD and microstructural analyses. In addition, the microhardness and fracture toughness of the samples were measured by the Vickers method at loads of 9.8 N and 294 N, respectively, and the density of the samples after sintering was determined by hydrostatic weighing. The highest relative density of 99% was obtained with EBS at 1450 °C for 4 min, while the relative densities of the sintered samples at 1250 °C and 1350 °C for 4 min and at 1450 °C for 2 min were 70 %, 81 %, and 89 %, respectively.

XRD analysis showed the presence of three phases (WC, bcc solid solution, and WC1-x) in all sintered samples. First, the presence of the HEA bcc solid solution should be noted, which shows the absence of significant interactions between the WC and binder. In addition, under all sintering conditions, the WC1-x phase is formed, which cannot be detected on the microstructure of the samples, unlike HEA. The appearance of this new phase may be associated with a high sintering rate and the presence of a thin oxide layer on the particles of components, which leads to reduction processes on the surface of the particles and the boundary between them [5]. The microhardness and fracture toughness of the samples, sintered at 1450 °C for 4 min, are 18.9 GPa and 11.4 MPa·m1/2, respectively. Thus, this study shows perspectives of nanostructured FeCrNiWMo HEA as a binder for cemented carbides with high microhardness and crack resistance of the alloy, while the short EBS time and slow diffusion of the HEA limit the growth of WC grains.

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Conference Track: “Nanomaterials Synthesis & Self-assembly” 01nssa-19
Spatially Nanoconfined Assembly of Indigo Carmine by Double Emulsion Technique

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Abstract ID #NSS- 0107

Spatial confinement has a great impact on directing molecular self-assembly. This approach has been attracting tremendous attention because it provides distinct advantages of obtaining designed materials with new functionalities [1]. Recently, we showed that the spherical cavity of polymeric nanocapsules provide a powerful confining system for self-assembly of organic dye molecules, indigo carmine, into nanoscrolls [2].

The nanocapsule formulations, were achieved by the double emulsion (water/oil/water) technique, comprised of amphiphilic polyether-polyester block copolymer (PEG-b-PLA), and copolymer based on meta-acrylic acid (Eudragit® S100) as a matrix polymeric capsule shell and loaded indigo carmine. The aim of this study was to evaluate and identify important formulation variables that often play a critical role in controlling encapsulation process and influencing the morphologies of the indigo carmine nano-emulsion system. The various factors, including polymeric composition, emulsifier concentration, polymer amount, oil phase volume, and solvent evaporation method during the solidification step were analyzed by the properties of nanocapsules, such as core content, particle size distribution, zeta potential, encapsulation efficiency and loading capacity. The nanoparticle formulations were characterized by advanced methods like cryogenic-Transmission Electron Microscope (cryo-TEM) and cryogenic-Electron Tomography (cryo-ET). Combined continuum theory and molecular modeling allowed us to estimate the material properties of the confined nanosheets, including their mechanical properties such as elasticity and brittleness. The results demonstrate a simple and useful route for constructing nanostructures of self-assembly by combination of spatial nanoconfinement strategy with double emulsion technique.

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REFERENCES

Impact of Interface Interactions on a Structure Formation of the Nanostructured Poly(Urethane-Urea) – Poly(Vinyl Chloride) Blends Filled with Modified Nanosilica

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Abstract ID #NSS-0137

Polymer blends and alloys in whole times attract significant attention of scientific community because of their ability to regulate precisely the functional characteristics of final materials [1-2]. Among the variety of such materials, a combination of elastomers and thermoplastics are result in very advanced materials due to a possibility of properties regulation in wide range. Coupling exhaustive polyurethane elastomer with chlorine-containing polyolefins provides dual positive achievements – strengthening of elastomeric matrix by dispersed thermoplastic phase and plasticization of rigid thermoplastics phase by flexible polyurethane elastomer chains. For commercial polymer blends another absolutely required component is an inorganic filler that possesses improved technological and exploitation characteristics by affecting the phase structure of the multicomponent system at micro- and nanoscale [2-4]. Earlier studies of polyurethane/poly(vinyl chloride) blends demonstrate great potential in changing the properties and wide perspectives of its practical uses [5-6].

Here we studied the effect of interfacial interactions between linear segmented poly(urethane-urea) (PUU) elastomers of different structures and thermoplastic poly(vinyl chloride) (PVC) in their compositions, as well as an impact of a nanosilica filler on the structuration of multicomponent polymer systems from the point of view of their key functional characteristics.

Dimethyldichlorosilane modified nanosilica has a minor destabilization effect on the Hydrogen-bonding network and reduces the tensile properties of PUU-1/PVC composites compared to the compositions filled with unmodified hydrophilic nanosilica. Otherwise, introducing modified filler into the PUU-2/PVC blend weakens intermolecular interactions at the interface and reduces the strength of filled polymer composites due to adsorption interactions of residual polar chlorine groups of nanosilica modifier at nanosilica surface and proton donor NH groups of hard segments of the PUU elastomer. At the same time, intra-component C=Oδ-…αHδ+ interactions were not changed under these experimental conditions. Thus, these interactions do not affect phase separation processes and functional characteristics of filled polymer nanocomposite films. It was found that the optimal content of the filler for PUU-1/PVC blend is up to 3 wt% of modified and up to 1 wt% of neat nanosilica, however for PUU-2/PVC blend a filler content could not overcome 1 wt%. So, the impact of interface interactions on tensile properties of nanostructured polymer blends depends mainly on the nature of nanosilica modifier and chemical structure of the poly(urethane-urea) matrix.

REFERENCES

Switchable Crystal Growth Mechanism in Zeolite Systems

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Abstract ID #NSS- 0144

Zeolites are crystalline microporous materials widely used in catalysis, adsorption, and separation [1]. Despite numerous studies aimed at understanding zeolite crystallization mechanisms, target-oriented control of zeolite crystals with unique structures or textural properties remains elusive [2]. Generally, zeolite crystal develops in a supersaturated solution, and their formation starts at the nucleation of discrete particles. A key feature of these “crystal nuclei” (the smallest entities) is the identity of the resulting crystalline phase. Then, these nuclei grow by deposition of low-molecular species, resulting from the dissolution of other crystalline or amorphous particles in the synthesis gel, thereby forming the final crystals. This mechanism is known as classical crystal growth [3]. In reversed crystal growth, nanocrystallites are integrated into large aggregates during the early stages of crystallization, followed by recrystallization from its surface to the center (contrary to the classical model in which growth starts from the nuclei). This recrystallization (i.e., formation of a crystalline phase from another crystalline phase) of aggregates in reversed crystal growth has been described in many systems, including zeolites, perovskites, metal oxides, and metal organic frameworks. In turn, crystallization from the surface of amorphous aggregates (i.e., formation of crystalline phase from the amorphous state) to their centers, instead of recrystallization from preformed crystallites, is a conceptually different mechanism of reversed crystal growth, which is still poorly understood and not observed in zeolite-type synthesis systems without additional confinement of starting materials within polymeric networks providing particular nucleation sites at the host-guest interfaces.

In this work, we present a novel model of reversed zeolite crystal growth in which crystallization starts at the surface of the amorphous aggregates. This initial step allows us to “switch” the crystal growth mode between classical and reversed routes based on the interplay between inorganic and organic components under specific synthesis conditions. By adjusting the template/silica and F/silica ratios in the synthesis mixture, we identified that the template plays a key role in controlling the crystallization pathway, whereas the concentration of F determines the rate of crystal growth. The type of mechanism and details of the inner structure of intermediate particles were confirmed by comprehensive electron microscopy studies of aliquots collected at different synthesis times. Furthermore, the development of the internal crystallinity of large aggregates (~ 60 μm) in the reversed crystal growth was visualized by nano X-ray tomography. The resulting understanding of this crystal growth mechanism and the development of an easy tool for its control are important for improving synthesis protocols and designing crystalline materials.

ACKNOWLEDGMENTS

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REFERENCES

Thermal Stability Of C/SiC Nanocomposites Prepared by the Two-stage Spray Pyrolysis Method from Selected Organosilicon Compounds

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The excellent properties of silicon carbide make it suitable for use in many modern technologies. In addition to extremely favorable mechanical properties, SiC has good thermal conductivity, semiconducting properties, and high thermal and chemical resistance. The high resistance to radiation damage combined with good thermal conductivity favors its use in the field of nuclear energy for the preparation of multilayer protective coatings for TRISO fuel. Thermal and chemical resistance determined the use of silicon carbide in solar radiation harvesting systems to generate electricity. Because of its very good thermal conductivity, it is also considered catalyst support in the synthesis of gas production reactions. In C/SiC composite systems, the silicon carbide coating improves the oxidation resistance of the carbon material.

Herein, presented are the results of a study on the thermal stability of the C/SiC nanocomposite powders obtained by the two-stage spray pyrolysis method from selected liquid organosilicon compounds. Details of the method were described in previous papers [1-3]. In this method, the precursor mist was transported by argon gas through the preheated tube reactor to undergo thermochemical changes. The resulting raw powders containing SiOxCy and carbon were collected in the filter attached to the output of the reactor. The raw powders were then heat-treated at 1650 °C in an argon flow to complete the carbothermal reduction of the silicon oxycarbide towards SiC. The powders were characterized by powder XRD, SEM, and FT-IR spectroscopy. The thermal stability of the final powders was estimated by TGA/DTA thermal analysis.

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REFERENCES

Graphene/Bi$_2$Se$_3$/ZnO Heterostructures with Enhanced Photoluminescence of ZnO Nanolayers

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The graphene/Bi$_2$Se$_3$/ZnO heterostructure is a new combination of high- and low-band gap nanomaterials that can be promising for application in optoelectronic devices. Due to the existence of surface plasmon resonance on the interface between ZnO and topological insulator, such as Bi$_2$Se$_3$, the photoluminescence of ZnO nanolayers can be enhanced. In turn, due to the very small lattice mismatch, graphene used as a substrate for Bi$_2$Se$_3$ synthesis influences the crystallographic growth of Bi$_2$Se$_3$ nanolayers [1]. The influence of the Bi$_2$Se$_3$ substrate on crystallization of ZnO nanolayers and charge separation at the Bi$_2$Se$_3$/ZnO interface may have impact on optical and electronic properties of the heterostructure.

In this work, the structure and optical properties of ZnO nanolayers were compared in relation to the substrate: graphene/Bi$_2$Se$_3$, quartz/Bi$_2$Se$_3$ and p-doped Si [2]. The charge separation at the Bi$_2$Se$_3$/ZnO interface, improvement of ZnO crystal structure and surface-plasmon-photon coupling were studied in detail for fabricated heterostructures with different ZnO nanolayers thicknesses (10-150 nm). Possible mechanisms of photoluminescence enhancement of ZnO nanolayers in Bi$_2$Se$_3$/ZnO heterostructures are proposed.

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Shortage of water is considered as one of the major challenges in a great number of countries. Under such condition, hydrogels can be used as an alternative way which helps to reduce the problem of water scarcity for agricultural applications. Hydrogels are unique hydrophilic polymer materials that can absorb and hold huge amounts of water even under changeable conditions of the environment.

The purpose of the study was development of organic/inorganic hydrogels based on sodium salt of polyacrylic acid (PAANa) and poly-N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (PAPTMS) with improved swelling and mechanical properties as well as studying of swelling kinetics and retention capacity to evaluate the possibility of hydrogels application as promising water reservoir materials.

PAANa/PAPTMS hydrogels were prepared by one-pot simultaneous cross-linking processing, which includes a combination of free radical polymerization of AANa (neutralization degree was 10 %) in a presence of N,N'-methylene-bis(acrylamide) cross-linker and hydrolysis of silica precursors with further catalytically-induced condensation of the resulting -OH groups of APTMS (from 5 to 20 wt.%). The cross-linking of PAANa was verified by the absence of C=C bond as well as network structure formation was performed by FTIR. The swelling capacity of the hydrogel was evaluated in distilled water, it was found that the incorporation of 10 wt% PAPTMS enhanced the water absorbency by 316% (from 16.81 to 70.22 g/g). The swelling behavior of the hydrogels is non-Fickian.

The PAANa/PAPTMS = 80/20 sorption curve differs from others, so for calculation of kinetics parameters the curve was interpreted as a result of a combination of two simultaneous processes: the first one that follows a first-order kinetics with a very small rate constant and the second one the overall autocatalytic process with its two rate constants. The autocatalytic mechanism of water-swelling was explained as the disruption of H-bonds starts after penetration of water molecules inside the sample and the decreasing of hydrophobicity of the medium occurs due to ionization of carboxylic groups. This means that the penetration of new water molecules will be easier because the medium becomes more hydrophilic. Despite the fact that the autocatalytic mechanism is in a good agreement with the experimental data, there is discrepancy on the initial stage of swelling. A first order equation was used to describe this stage. The combination of two mechanisms at 80/20 ratio (contribution of autocatalytic process is 80%) gives the best fitting.

Received data allow concluding that synthesized hydrogels show enhanced swelling capacity and can be considered as promising water reservoirs. The incorporation of PAPTMS into the polymeric matrix confirmed by FTIR spectroscopy and its amount greatly influences on swelling/deswelling kinetics and swelling ratio.
Green Synthesis of Silver-Containing Biomaterials with Effective Antimicrobial and Antiviral Activity

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Despite the rapid progress in drug development and pharmaceutical technology, infectious diseases caused by microorganisms and viruses continue to be one of the biggest health problems in the world. In particular, the evolution of microorganisms such as Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa, fungal pathogens Candida albicans, etc makes them resistant to known antimicrobial agents. The spread of viral infections, including COVID-19, influenza A virus, herpes simplex virus 1, and adenovirus serotype 2, is also a problem. Recently, the development of antimicrobial and antiviral materials based on biopolymers filled with nanoparticles of silver, copper, and zinc oxide attracted the most attention. There are a lot of data about the antimicrobial activity of polymeric biocomposites with silver nanoparticles with size ranges of 10–100 nm. The aim of this work is the green synthesis, characterization, and assessment of antimicrobial and antiviral properties of biomaterials (powders, films, solutions) with silver nanoparticles in ultrafine size (d <10 nm).

Powdered silver-containing materials based on polyelectrolyte complexes with the participation of polysaccharides (pectin – chitosan, pectin – cationic starch, carboxymethylcellulose (CMC) – cationic β-cyclodextrin, anionic starch – cationic starch) were developed [1]. Silver-containing film materials based on polylactide biopolymer were created in three ways: (i) reduction of Ag+ ions by using green tea extract in solution of PLA with AgPalm; (ii) thermochemical reduction of Ag+ ions in PLA-AgPalm-chitosan polymer systems; (iii) cathodic sputtering of Ag nanoparticles from silver foil on the surface of the PLA [2, 3]. Silver-containing solutions (sprays) were synthesized by reducing silver ions with green tea extract, mint extract, propolis extract, and pectin. The obtained materials were characterized by FTIR, WAXS, TEM, TGA, DSC, and mechanical methods, and their antimicrobial, antiviral and cytotoxic properties were studied. The relationship between the structure, morphology, antimicrobial and antiviral properties of the obtained materials was studied.

The elaborated materials can be promising for the treatment of wounds of various infectious origins; for the formation of antimicrobial coatings in medical, pharmacological, and biological laboratories to ensure sterile conditions; for creating packaging materials for long-term, high-quality and safe storage of food; as antimicrobial air filters in ventilation systems in hospitals and microbiological laboratories; for creating medical masks, etc.

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REFERENCES


Laser Growth of Multi-Walled Carbon Nanotube Thin Films

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Abstract ID #NSS- 0164

Pulsed Laser Deposition (PLD) is a process in which laser radiation is used to "knock out" carbon materials from the surface layers of the target and apply them to the substrate to form stoichiometric single and multilayer coatings with special properties. Today, PLD technology is of great interest in industries such as microelectronics, micro- and nanophotonics, as obtaining high-quality film structures is a priority in these areas. Neodymium KGd(WO4)2: Nd laser was used in our experiment. used with parameters: λ = 1064 nm, pulse energy 0.5 J, power density 100 MW/mm², pulse duration: in the mode of modulated quality factor - 20 ns, in the mode of free generation - 200 μs; section of a bar of 3 mm. The films Multi-Walled Carbon Nanotubes (MWCNTs) were obtained in two ways. The first method is to spray the film in a vacuum. To do this, place the substrate (glass, silicon, quartz) on a platform in a vacuum chamber on which the films will be sprayed. We use carbon fiber as a target [1].

For the analysis of films, their absorbency was measured in the wavelength range of 200-3000 nm on a spectrometer. The absorption capacity of light is characterized by a coefficient called absorption A (this is the product of the absorption coefficient by the film thickness). Absorption is determined by the ratio of light intensity (in particular, input I0 and output I). That is, ln (I/I0) = A, the parameter depends on the wavelength of light. If the absorption is represented not by the wavelength but by the energy of the photons of light (E = 1240/λ, λ is the wavelength), we can estimate the energy of the photons of light at which there is a sharp diffusion of light. absorbing layer. This physical effect is one of the methods of identifying both the material and its structure. From the experiment it was found that this energy is 4.5 electron volts. Comparing with the literature [2, 3], we can say that the resulting thin carbon film has one of the structural modifications of the graphene-like structure. The second method of obtaining nanoclay films was the direct melting of carbon into the glass surface. The carbon nanoparticle powder was poured on a substrate (glass plate). The workpiece was then placed in the area, whether it is a graphene film, it can not be determined by visual observation under a microscope. However, it is known that the presence of a surface film of graphene leads to an increase in the microhardness of the material. Therefore, we measured the microhardness on a clean glass surface and on a film surface. The following results were obtained: on a clean surface HV = 6 GPa, on a film - HV=7.2 GPa. Therefore, it can be assumed that the film obtained on the glass surface may have a graphene-like structure.

REFERENCES

Hybrid Biopolymer Nanocomposite Materials for Ecological and Biomedical Applications

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Abstract ID #NSS-0168

In the last 10-15 years, hybrid polymer nanocomposite materials with biological activity have become widespread [1, 2]. They have important areas of application not only in modern nanomedical technologies and drugs, but also in the processes of purification and bioremediation of hydrocarbon-contaminated various environmental objects, adsorption, separation and storage of gas, catalysis, sounding, electronic devices and more. Such polymeric hybrid nanocomposite materials have attracted attention due to their special structural and surface characteristics, which determine such a wide range of functional applications. A perspective direction for the design of hybrid polymer nanocomposite materials based on functional hybrid modification of polylactide with humic substances. Mixtures of polylactide with humic substances are interesting because of their potential application as biomedical frameworks for the production of adsorbents of pollutants and heavy metal ions, antibacterial biomaterials, drug delivery systems, sorbents of oil-containing natural, industrial and domestic waters, etc. In our previous works [3, 4] we studied humic substances as structuring and antimicrobial agents in different types of biopolymers.

The purpose of this work was to study hybrid biopolymer nanocomposite materials for ecological and biomedical applications. The objects of study were plastic bland of PLA Terramac TP–4000 and humic substances, which were obtained by extraction of brown coal.

The processes of extraction of humic substances from brown coal were studied by four different methods, it was found that for the extracted nanodisperse particles of humic substances the size is from 52 nm to 380 nm. The size distribution in the submicron region in solutions of all humic substances is unimodally wide and, therefore, polydisperse, which it is based on the value of the index of polydispersion, which ranges from 0.38 to 1.00. It was found that the presence of these functional groups determines the ability of humic substances to act as a hybrid modifier in relation to polylactid: conformational changes in its secondary structure and dipole-dipole interaction in the form of a hydrogen bond. Due to the increase in the degree of crystallization and the emergence of intermolecular and ester bonds in the formation of a more rigid network structure in the polylactid-humic substances system there is an increase in mechanical properties of hybrid biopolymer nanocomposite materials.

Designed hybrid biopolymer nanocomposite materials based on polylactide and nanodisperse humic substances were used as highly effective sorption materials to reduce heavy metal ions in oil natural, industrial and domestic waters and dosage forms in the production of drugs for the removal of heavy metal ions from the human body.
Effect of Surfactants on the Synthesis of NiFe$_2$O$_4$/rGO Composites by co-Precipitation Method

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The effect of the surfactants (polyethylene glycol (PEG-6000), Trinon X-100 (TrX-100) and cetyltrimethylammonium bromide (CTAB)) on the structure of NiFe$_2$O$_4$/rGO composites was studied. Colloidal GO was synthesized by Hummers method and used for NiFe$_2$O$_4$/rGO composites obtaining via co-precipitation route. Hydrazine hydrate was simultaneously used as pH increasing and GO reduction agent. The next systems were obtained: X0-GO free, no surfactants were used; X1-GO presence, no surfactants; X2-GO presence, PEG-6000; X3-GO presence, CTAB; X4-GO presence, TrX-100. GO consists of particles of graphene oxide with an average thickness (D) of 5.6 nm. The hydrazine-induced reduction causes the removal of surface functionality and leads to interplanar distance shrinking to 0.38 nm and $D=1.3$ nm. X0 sample has a single-phase NiFe$_2$O$_4$ spinel structure with particle sizes of 22 nm. X1 and X2 have a high structural disordering and consist of NiFe$_2$O$_4$ and a-Fe$_2$O$_3$ phases. CTAB and TrX-100 assisted synthesis (X3 and X4) leads to ultrafine spinel formation. The annealing at 500°C causes growth of particles but in both X3-500 and X4-500 materials consist of ultrafine NiFe2O4 only with particle sizes of 8-9 and 6-7 nm, respectively. The nucleation of the co-den-sed phases from the solution of metal (M) salts involves the stages of hydrolysis, metal hyd-ro-complexes formation and polycondensation. The metal ions hydro-lization processes leads to the formation of $[M(OH)_{h}(OH_2)]N-h^+\_h$ complexes, where N is the coordination num-ber, z is the oxidation deg-ree and h is protolysis degree. The changing of pH and appropriate changes of hyd-rolysis degree allow control the olation interactions between hydrocomplexes that predetermine the nucle-a-tion of a new phases. The formation of spinel nuclei starts at pH>7 and most effective at pH>10. The presence of GO leads to the disordered two-phase system (NiFe2O4 and a-Fe2O3) formation due to the electrostatic interaction between the $[Fe(OH)(OH_2)_{4}]^{2+}$ hydrocomplexes (at pH<5) and the hydroxylated surface of GO when GO particles becoming centers of nucleation of the hematite. PEG molecules are immobilized at the edges of the graphene planes only without participating in the oxide phases nucleation. [CTAB]$^+$ cationic complexes are electrosorbed on the surface of GO graphene oxide particles, limiting the interaction between iron hydrocomplexes and reducing the probability of a hematite formation at pH < 5–7. The pH growth decrease of [CTAB]$^+$ concentration on the GO that promote of low-agglomerated NiFe$_2$O$_4$ particles (8-9 nm) nucleation. TrX-100 molecules are adsorbed on the hydroxylated surface of GO through octyl groups with the spatial limiting the interaction between electrosorbed hydrocomplexes of Fe and Ni with suppression of hematite nucleation. As a results, the ultrafine composite materials is formed consisting of NiFe$_2$O$_4$ particles (6-9 nm) located on rGO particles of with average lateral length of about 12 nm.

Conference Track: “Nanomaterials Synthesis & Self-assembly” 01nssa-29
Fabrication and Characterization of Unique Double-sided Semitransparent Photoelectrode Composed of Ordered Nanotubes

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Novel and efficient supercapacitors, water-splitting devices or batteries with high capacitance, as well as various sensors are hot topics within the society and their intensive development take advantage from the nanomaterials. Because of the highly developed surface area, much more charge can be accumulated at the surface while the further modification can bring us highly sensitive substrate. Among others, titania nanotubes prepared via anodization provide well ordered, developed surface as well as exhibit stability and resistance towards photoelectrochemical corrosion. Therefore, this material can find application as a promising electrode material for energy conversion, storage and detection of selected species.

Up to now titania nanotubes were formed on the titanium foil, wires, tubes or titania layer deposited onto conducting substrate. In the former case when Tin oped Indium Oxide (ITO) or Fluorine doped Tin Oxide (FTO) is used as platform for Ti sputtering, as the result of anodization one may obtain semitransparent, ordered titania nanotubes. However, only on one side of such flat substrate ordered titania has been formed. Herein, we propose fabrication of the unique double-sided flat electrode, where on both sides of glass plate conducting ITO is overgrown by ordered titania. The optimization of the ITO layer, thin titania layer and finally 0,5-1 µm of Ti deposition provides us substrate for the anodization process. Owing to the special sample holder and numerous trials, we elaborated the method of the double-faced electrode material fabrication. The presence of ethylene glycol in anodizing bath enables us to form aligned nanotubes while diethylene glycol provides free space between tubes. Following that, starting from Ti/ITO present on both sides of glass slide we can finish with separated or aligned nanotubes on both sides or as an anodization result the mixed arrangement can be reached, namely one side can be covered by aligned tubes while on the opposite one the free space between tubes can be achieved. The top-view and cross-section morphology was investigated using Scanning Electron Microscopy (SEM). The control of the nanoarchitecture affects the optical properties that were investigated by means of UV-vis spectroscopy.

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Developement and Characterization of Aluminum Incorporated Diamond-Like Carbon Thin Films at Varying Deposition Temperatures

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The present work deals with the study of various properties of Aluminium (Al) incorporated Diamond-Like Carbon (DLC) thin films synthesized over Si (100) wafer using Atmospheric Pressure Chemical Vapour Deposition (APCVD) technique with variation in deposition temperature and keeping the N2 flow rate constant. The analysis of surface morphology, resistance to corrosion, nano hardness (H) and young’s modulus (E) of the thin coatings is carried out by Atomic Force Microscopy (AFM), corrosion test, Scanning Electron Microscopy (SEM) and Nano-Indentation. SEM results showed smoother surface morphology of the coatings grown at different process temperatures. With an increase in process temperature, the coating roughness (Ra) lies in the range of 20 to 36 µm. The corrosion resistance of the coating found to be reduced with a consecutive increase in the deposition temperature and this could be due to higher randomness of gaseous molecules at high temperatures. The nanoindentation result revealed that the coating H and E increase with enhancement in CVD process temperature. The elastic-plastic property indicated by H/E and H^3/E^2 which is also an indication of wear properties of the coating are studied using the nanoindentation technique. The residual stresses calculated by using Stoney’s equation revealed a reduction in residual stress with an increase in the process temperature.

REFERENCES

Germanosilicates as Extended Building Units for the Rational Synthesis of New Zeolite Catalysts

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Abstract ID #NSS-0201

Aluminosilicate zeolites represent the most important heterogeneous catalysts with a high number of large-scale industrial applications. Due to a great plethora of possibilities for utilization of zeolites as tailor-made catalysts, the synthesis of novel frameworks and modification of the properties of well-known zeolites are still the key targets. However, the formation of most of theoretically predicted zeolites with unusual structural characteristics was shown to be unfavourable under equilibrium conditions [1]. As an alternative to conventional hydrothermal synthesis, we proposed the ADOR strategy for interzeolite conversion (including Assembly-Disassembly-Organization-Reassembly steps), which benefits from the irreversibility of the final material-forming step [2]. The ADOR method is based on a complex sequence of steps that include (i) controllable acid-base-catalysed water-assisted degradation of hydrolytically unstable bonds in the zeolite framework followed by (ii) reorganisation of the silica building units formed, and (iii) their topotactic condensation into a new framework with a topology closely related to the original one. The critical prerequisite responsible for this behaviour is the presence of regions of different compositions (i.e., silica layers supported by Ge-enriched D4R units) in the original zeolite.

This work exemplifies the success of the ADOR approach for UTL, UOV, IWW, and *CTH germanosilicates, which were transformed into new zeolites inaccessible by direct hydrothermal synthesis. The type of linkage in the derived zeolites strongly depends on the synthesis conditions, which affects the relative rates of leaching, diffusion, and reinsertion of germanate and silicate ions or polyatomic species [3-4].

In addition to transformations involving structural alteration of germanosilicate zeolites, their framework composition was adjusted while maintaining the zeolite structure. Specifically, Ge framework atoms were substituted with Al, Ti, Sn, and Zr by post-synthesis treatment using consecutive degermanation and heteroelement insertion steps, optionally with intermediate incorporation of silicon for framework stabilization. These subprocesses have been studied in detail and optimized to prevent deposition of extracted germanium-containing species or incorporation of heteroelements into extraframework positions. The developed methods for incorporation of various heteroelements allowed us not only to improve hydrolytic stability but also to generate acid sites of different nature, known as active centres in various acid-catalysed reactions.

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Colloidal Properties of Amorphous Silicas Synthesized by Fluoride and Pyrogenic Methods

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Due to the wide range of amorphous highly dispersed silica applications, research on the development of new resource- and energy-efficient technologies for the SiO2 synthesis is of great interest both to researchers and consumers of this product. The aim of the study was to investigate the properties of the amorphous silicas, synthesized from metallurgical waste using the fluoride method (Slags from the copper-smelting production of the Almalyk Mining and Metallurgical Combine (AMMC)) (SiSlag, SBET = 64 m2/g) and microsilica (MS, dusty wastes from the production of FeSi65 of Uzmetkombinat JSC ((SiMS, SBET = 11 m2/g) as well as to analyze and identify their features in comparison with A-60 silica synthesized by the pyrogenic method (SBET = 80 m2/g, Pilot plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine). This approach would reveal the effectiveness of the application of non-traditional methods of synthesis and at the same time using non-standard and cheap raw materials, including technogenic metallurgical wastes and for its turn also may serve as a solution to some problems associated with environmental pollution [1].

It was found that A-60 has the highest adsorption capacity with respect to methylene blue (A_{max} = 15 mg/g). This may be due to the larger specific surface area of this sample. SiSlag silica sample has a lower adsorption activity (A_{max} = 10 mg/g) due to the smaller specific surface area and the significantly higher amount of adsorbed water, that remains as a result of synthesis. The heat of immersion in water (as a polar liquid), calculated per m2 of its surface, is higher than for A-60 and SiSlag. The hydrophilicity indexes of samples SiSlag and SiMS are 10 and 20, respectively, which is significantly higher than for pyrogenic silica A-60, for which Kh = 2. It was revealed that for SiSlag zeta potential is positive +1,92 mB and +14,1 mB for SiMS in an acidic medium (pH = 2.70-2.78, CSiO2 = 0,02 %wt.). When the pH of the medium changes to alkaline (range from 3 to 12), a reversal of the zeta potential to negative values is observed and increase in absolute value from 0 to 37.8 (SiSlag) and 15,7 mB (SiMS). The dependence of the zeta potential vs pH for A-60 practically coincides with the curve for SiSlag. This can be explained by the presence of ionogenic hydroxyl centers on the silica surface. It is the surface density of ionized centers that is responsible for the specific charge of the silica surface. It has been shown by laser correlation spectroscopy that for all the studied silica samples the particle size distribution is bi- and tri-modal; the particle diameter is predominantly 1300 and 5500 nm in an aqueous medium. The effective diameter of the silica particles decreases with increasing the ultrasonic treatment time. Thus, a silica samples, synthesized by the fluoride method have similar properties to A-60 and can be used as sorbent, carrier, filler and as a thickener for paints, adhesives and sealants.

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Synthesis and Properties of Layered Materials Based on Epoxy Binder Reinforced with Carbon Nanotubes and their Oxygen-modified Forms

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The interaction of the epoxy component of fiberglass with the surface of the nanocarbon filler (multiwall Carbon Nanotubes (CNTs)) was studied [1]. It is established that the highest strength values of epoxy composites are achieved by adding the initial multiwall carbon nanotubes into the epoxy composition hardener, and it is much more efficient to use oxidized CNTs, when modifying the resin. The optimal value of the total content of CNTs (about 1% wt.) in terms of solid resin was determined, at which the tensile strength of the composite is maximum.

Quantum chemical calculations of the interaction of initial and oxidized models of the surface of a multiwall CNTs (graphene-like planes) with a molecule of a hardener (triethylenetetramine) were performed. It was found that regardless of the size of the graphene-like plane, the energy of intermolecular interaction of triethylenetetramine with the model of the oxidized outer surface of multilayer CNTs is greater than the same value for complexes with non-oxidized. Thus, the oxidized surface of the nanotube impairs the interaction of the hardener with the epoxy resin in the formation of a 3D polymer lattice of the finished nanocomposite, which is confirmed by experimental data [2].

Oxidized nanotubes due to acid groups on the surface return the molecules of the hardener amino groups to the surface of CNTs, and hydrocarbon residues to the outside, i.e. does not form a charged layer that would prevent agglomeration. Due to this orientation of the amino group, the hardener molecules are adsorbed on the surface of CNTs, i.e. screened by their own hydrocarbon residues from the epoxy groups of the resin during curing (which weakens the bond of CNTs with the polymer matrix). In the case of dispersion of oxidized CNTs in the resin, the oxygen-containing groups on the CNTs surface due to their polarity prevent reverse agglomeration after dispersion. In addition, it is known that organic OH-groups are a catalyst for the polymerization of epoxy resins, capable of activating epoxy groups and causing the transition complex in the reactions of the amine hardener with epoxy resin. This mechanism obviously works with surface OH-groups of oxidized CNTs, which contributes to a faster and more complete process of forming a 3D structure of the epoxy composition in the case of adding oxidized CNTs to the epoxy resin.

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Synthesis & Characterization of ZnO and RE-doped ZnO Nanofibers

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Abstract ID #NSS- 0210

Doping of the zinc oxide crystal lattice is considered to be the most effective and the most widely used method, the aim of which is most often to improve the physicochemical properties of ZnO nanostructures [1]. Many application possibilities of zinc oxide-based nanomaterials depend primarily on the size of crystallites, stresses in the crystal lattice caused by the presence of atoms and/or ions of foreign elements, and the extent of electromagnetic radiation absorption resulting from the concentration and form of admixtures [2]. Lanthanides are one of the groups of elements to which much attention is paid as structural impurities of ZnO, mainly due to the much better optical properties of the obtained hybrid nanomaterials [3].

Pure and RE-doped ZnO (RE = Yb$_2$O$_3$/Yb$^{3+}$, Eu$_2$O$_3$/Eu$^{3+}$ and (Eu$_{1.6}$Yb$_{0.4}$)O$_3$) one-dimensional nanostructures were produced using electrospinning of thin polymer-ceramic fibrous mats followed by high-temperature heat treatment at 500 °C for a period of time 3 hours. The surface morphology analysis of as-spun fibrous polymer-ceramic mats was carried out using SEM and an X-ray Energy Dispersive detector (EDX), which showed no structural defects in the material. One-dimensional ceramic nanostructures were characterized in terms of morphology (SEM, TEM) and structure (HRTEM, XRD, FTIR), and the performed analysis showed the highly crystalline nature of ZnO and hybrid nanofibers with mixed phase structure. The use of the Halder-Wagner (H-W) method allowed to determine the average crystallite size of the analyzed ceramic nanofibers, which ranged from 14.2 to 35 nm. The calculations of the stresses of the crystal lattice of the studied nanostructures showed an increase in stresses caused by the doping of rare earth metals in the structure of the ZnO crystal lattice.

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Ammonium Vanadate/Reduced Graphene Oxide Composites: From Fabrication to Application

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Abstract ID #NSS-0229

Composites fabricated from vanadate-based compounds and carbonaceous materials have gained extensive attention due to their potential applications in electrochemistry and photocatalysis. Vanadates pose specific layered structure which, together with multivalent nature of vanadium, make them potential candidates for electrode material in mono and multivalent ion batteries [1, 2]. In addition, large majority of vanadates absorbs visible light and have been widely investigated in solar-driven photodegradation of organic pollutants or water splitting [3, 4]. However, their practical application is still hindered, mainly due to the low electrical conductivity and insufficient structure stability. One of the solutions for the mentioned limitations is combining vanadates with well-conductive reduced Graphene Oxide (rGO). RGO not only improves the electron transport but also ensures structure integrity and increases specific surface area improving mass-transport and access to active sites. It is also known that rGO prevents charge recombination, which is beneficial for photocatalytic performance.

The presented research is focused on the composites based on Ammonium Vanadates and reduced graphene oxide (AVs/rGO). Unfortunately, the detailed experimental characterization for such novel composites is still lacking in the literature. Thus, the ultimate goal of this study was the synthesis of AVs/rGO composites and their physicochemical characterization. Herein, we demonstrate for the first time the effect of the synthesis parameters (such as precursor ratio, pH, concentration of GO solution) on the final AVs/rGO composites structure.

Samples were obtained via facile hydrothermal method (8h, 180°C), which includes simultaneous reduction of NH₄VO₃ and graphene oxide to AVs (e.g. NH₄V₄O₁₀, NH₄V₃O₉) and rGO. During this reaction components self assemble into hierarchical composite microstructure, in which AVs can be anchored, encapsulated or wrapped with rGO sheets. Obtained AVs/rGO composites were fully characterized by means of XRD, SEM, FTIR, XPS, UV-Vis, TGA and N₂ adsorption. Various synthesis conditions resulted in different AVs phase composition and V⁴⁺/V⁵⁺ ratio as well as different composites morphology and surface area. Finally, selected composites were tested as cathode materials for Li-ion batteries. Moreover, their practical application as visible light-driven photocatalysts was presented for the first time. This was confirmed by efficient photodegradation of methylene blue and photoreduction of Cr(VI).

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Curing Kinetics of Cyanate Ester Resin in the Presence of Different Inorganic Nanoparticles and Thermal Properties of the Nanocomposites Synthesized

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Abstract ID #NSS-0235

In the present study, the kinetic peculiarities of Dicyanate Ester of Bisphenol E (DCBE) polycyclotrimerization to high performance Polycyanurate (PCN) in the presence of different type of nanoparticles were investigated by DSC technique. The amino-POSS, viz. aminopropylisobutyl POSS (APIB-POSS), aminoethylaminopropylisobutyl POSS (AEAPIB-POSS), N-phenylaminopropyl POSS (NPAP-POSS), as well as fullerite C60 of 0.1 wt.% content were used as nanofillers. The investigations were performed using DSC 25 Differential Scanning Calorimeter in nitrogen atmosphere by heating from 25 to 350 °C at a heating rate of 5 °C/min. For estimating glass transition temperatures (T_g) of the neat PCN synthesized from DCBE, and PCN-based nanocomposites, the second DSC scans with the heating rate of 20 °C/min over the temperature range from 50 °C to 350 °C in nitrogen atmosphere were performed.

The catalytic effect of the amino-POSS chosen was found for all the nanocomposites developed. The values of the exotherm peak temperature (T_p), reaction enthalpy (∆H), and the values of glass transition temperatures (T_g) of the cured PCN-based nanocomposites were determined. It was established that for the neat DCBE sample, a T_p value was equal to ~261 °C. For the DCBE/amino-POSS compositions the corresponding T_p values shifted toward much lower temperatures, viz. to T_p ~ 241–244°C in dependence on the type of amino-POSS. In a contrary, for the DCBE/C60 composition the T_p value shifted toward higher temperature up to T_p ~275°C. Furthermore, the enthalpy of the cure reaction ∆H for the neat DCBE was calculated to be ∆H ~ 842 J/g and it decreased significantly (to ∆H~678-786 J/g) depending to nanofiller type for all the nanocomposites studied. The catalytic effect of the amino-POSS is also confirmed by the temperature dependencies of the conversion (a) of cyanate group of DCBE because for the DCBE/amino-POSS nanocomposites the reduction of induction period of the reaction was observed and the polymerization started early. In a contrary, for the DCBE/C60 nanocomposite the induction period increased. It was found also that all the cured nanocomposites possessed high T_g values, which varies from 274 °C to 281 °C depending on the composition. At that, the DCBE/amino-POSS nanocomposites are characterized by the same T_g value as the individual PCN (T_g >> 274°C). In a contrary, the PCN/C60 nanocomposite exhibits the higher T_g values by 7 °C compared to that for the neat PCN.

Thus, the thermal polycyclotrimerization of DCBE is catalyzed by the reactive amino-functionalized POSS that provides polymerization of DCBE at lower temperatures; however, the amino-POSS studied do not affect the T_g value of the PCN synthesized. In its turn, the inert fullerite C60 does not accelerate the DCBE polymerization, but increases T_g value of the resulted polymer network.

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Effect of Iron Oxide/Reduced Graphene Oxide Hybrid Structure on Morphology and Properties of Epoxy Nanocomposites

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The use of particulate conductive fillers (metal compounds or carbon particles) in an electrically insulating polymer is a simple way to initiate electrical conductivity therein and, finally, produce Conductive Polymer Composites (CPCs). These composites are easy to process and characterized by tunable electrical properties ($10^{-8}$–$10^6$ S/m), enhanced mechanical properties, and relatively low manufacturing costs, making CPCs a promising research topic for academic and industrial communities [1]. Furthermore, recent trends show that the tailored hybrid fillers improve both thermal and electrical characteristics of composites more advantageous than in the case of individual fillers. Hybrid fillers for this purpose can be used in metal-carbon, metal-metal, or carbon-carbon combinations [2]. Hybrids with magnetic properties are particularly interesting as fillers for polymer composites. These magnetic materials under a magnetic field allow obtaining composites with an oriented arrangement of these particles, which results in better electrical conductivity, thermal conductivity, and other characteristics of CPCs [3, 4].

The aim of this work was to determine the relationship between the structure of hybrid fillers based on reduced Graphene Oxide NanoPlatelets (GNPs) coated with iron (III) oxide Nanoparticles (NPs) prepared using three different procedures and properties of epoxy composites with these fillers. The iron oxide NPs were synthesized and deposited on the graphene surfaces by (1) one-step direct co-precipitation and (2) homo-precipitation routes. In the third method, Fe$_2$O$_3$ NPs were functionalized with 3-aminopropyltrimethoxysilane and then attached to graphene surfaces. The structure of graphene layers and iron oxide crystalline phase forming hybrid fillers was determined by X-Ray Diffraction (XRD), Raman spectroscopy, and Scanning and Transmission Electron Microscopes (SEM-EDS, TEM). Two types of epoxy composites were prepared and characterized in the term of thermomechanical properties and electrical conductivity: (1) with a random distribution of hybrid fillers by typical mechanical and ultrasonic mixing methods and (2) and with a partially arranged distribution of fillers forced under external magnetic field (~0.5 T). The partial arrangement of graphene sheets coated with IO NPs was confirmed by the decreased area ratio of D to G bands in Raman spectra of composites. The effect of hybrid structure based on graphene nanoplatelets decorated with iron (III) oxide was obtained using various preparation procedures, and the content of filler NPs on percolation threshold of electrical properties and thermal stability, glass transition temperature, and dynamic elastic modulus was studied. The influence of magnetic treatment on the properties of epoxy composites was also studied in terms of their applicability as thermally and electrically conductive polymer composites with enhanced mechanical strength.

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Synthesis and Characterization of SiC-Based Thin Film Heterostructures

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One of the main tasks of physical materials science is to obtain nanoscale materials and structures that are promising for the development of new devices. In recent years, HeteroStructures (HS) combining film oxide coatings with silicon technology have become of particular interest. Of interest from the physical point of view is the ZnO/Si HS, which integrates the advantages of high binding energy of the ZnO thin film and the cheapness of Si substrates. However, in the cultivation of this structure, there are a number of inconsistencies caused by the structural mismatch between silicon and zinc oxide. It is proposed to use buffer layers to resolve this discrepancy. One of the options for intermediate layers may be a film of silicon carbide.

In the first stage, single-crystal Si plates of orientation (100) of the p-type conductivity were subjected to anodic etching in a solution of hydrofluoric acid HF. In the next step, silicon carbide layers were synthesized on mesoporous Si samples by the method of atom substitution. To do this, the samples were annealed in an atmosphere of a mixture of gases of carbon monoxide (CO) and silane (SiH\textsubscript{4}). The final step was the deposition of ZnO films by spraying a zinc target at RF discharge power in argon with oxygen. Target parameters: diameter 80 mm, thickness 6 mm, purity of Zinc 5N. Target-substrate distance 70 mm. Prior to deposition, the target was pre-sprayed for 10 minutes to remove all contaminants. The samples were divided into two groups, depending on the conditions of the deposition process.

The structure of SiC films was studied on an EMR-100 electron graph in the "reflection" mode at a fast voltage of 75 kV. The point reflexes of this electrogram unambiguously indicate that the SiC epitaxial layer lies on the Si surface. Characteristic circles corresponding to the polycrystalline phase are practically absent, but Kikuchi lines are clearly visible, which indicates the high quality of the crystal structure of the films. After magnetron sputtering, the surface of the studied samples is covered with a continuous film of ZnO. The formed film has a columnar structure, and the surface of the film is almost smooth and homogeneous, but it should be noted that the size of ZnO series two crystallites is almost four times larger and has a smaller scatter in roughness compared to samples of series 1. This fact indicates growth. The ZnO film on all samples is closely bound to the SiC/porous-Si/Si substrate. The SiC layer is slightly reduced from the original 100 to 80 nm.

Diffractograms of ZnO/SiC/porous-Si/Si samples with different oxygen concentrations will be presented. The presence of a triplet in the range of 31-36 degrees indicates the presence of a polycrystalline hexagonal phase of ZnO. In many cases, the mean reflex (002) dominates the diffractograms, which indicates the texturing of the material. However, in this case, such an effect is not observed.
Effect of Concentrated Light on Properties of Composite Powder Based on Boron Nitride

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Abstract ID #NSS- 0264

Heating under effect of concentrated light in any desired atmosphere of the optical furnace has a number of advantages and has been used to produce extremely high purity materials. This technique is also suitable for both conducting and non-conducting materials. High heating and cooling rates, versatility and ability to adjust temperature profile along each axis, maximum operating temperatures and environmental adaptability are the other important advantages.

The effect of adding 25 wt % of different powders (such as Ta, Hf, Cu, Zr, Ni, Al, Ti, Cr, or Fe) to boron powder on transformation of boron in a high-flux optical furnace in nitrogen flow was considered. Composite powders based on BN was prepared at the low-density energy in focal zone of set-up ~ 0.7 \times 10^4 \text{ kW/m}^2. Time of the experiment was 30 min.

It was demonstrated by the method of X-ray diffraction study (diffractometer “DRON-3.0”, radiation of K\(\alpha\) – Cu) that the phase composition of the prepared powders strongly depends on the ability of boron to form one or more borides when it reacts with most of the above-mentioned metals. Resulting structures of the composite powders based on BN, which were examined by transmission electron microscope JEM-2100F and scanning electron microscopy Superprobe-733 (electron beam diameter of 0.7 nm) also emphasize their dependence on the ability of boron to form borides.

Infrared spectra which were recorded by Nicolet 6700 FTIR spectrometer (frequency range of 650-4500/cm) equipped with a Thermo Nicole Continuum microscope and Raman scattering confirmed a complicated structure and phase composition of the powders with a prevalence of the amorphous phases. By Electron Paramagnetic Resonance (EPR), the features of structural transformations in composite powders were studied. A correlation between the dynamics of redistribution of the integral intensities of EPR signals and the structural parameters of the composite powders based on BN was revealed. Resonant frequency of atomic nuclei according to its chemical composition or environmental surroundings was characterized by the method of Nuclear Magnetic Resonance (NMR). Therefore, additives to boron powder effect on transformation of boron in a high-flux optical furnace in nitrogen flow on phase composition, morphology and structure formation.

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Carbon Nanotubes Growth in Converted Gas Atmosphere on Dispersed Iron Catalyst Obtained as Result of Ferrocene Decomposition

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This study aimed to obtain Carbon Nanotubes (CNTs) on an iron catalyst formed from the decomposition products of ferrocene in a converted gas atmosphere.

In the course of the study, an attempt was made to evaluate and test on a laboratory scale the technology for producing CNTs by the Chemical Vapour Deposition (CVD) method using ferrocene decomposition products as a catalyst. The products of air conversion of natural gas served for CNTs synthesis. Target carbon was obtained by disproportionation of carbon monoxide. The temperature regime for CNTs growth was about 650 °C and was chosen as optimal for the iron catalyst. Only precise control of the composition of the gas mixture and the ratio of the carbon source – carbon monoxide to hydrogen, as well as the temperature regime allows CNTs obtaining practically without external carbon impurities in the form of amorphous carbon.

Experiments have shown that dispersed iron particles obtained from ferrocene have a high reactivity, in many respects not inferior to freshly reduced iron, which, due to its low reduction temperature, has a developed surface and, as a consequence, is one of the most effective catalysts for carbon deposition. But the process of preparing such a catalyst is a rather laborious and energy-consuming process, which consists in multiple repetitions of oxidation-reduction cycles in order to obtain the most developed substrate surface for CNT deposition.

As a percentage of one unit of iron, approximately 14 weight units of carbon were obtained in the form of CNTs. The results on the yield of the target carbon product confirmed the possibility of using ferrocene as an effective catalyst for the growth of CNTs, as well as the possibility of using this technology on an industrial scale.

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Nanocomposites Poly(o-anisidine)-Graphene Oxide

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Developing new nanosized composite materials based on conducting polymers doped by inorganic clusters and studying their electrical, optical, and sensory properties becomes an important task. One of the most interesting conjugated polymers is Poly-o-Anisidine (PoA), which has high electrical conductivity and shows stable electrochemical and electrochromic characteristics, making it attractive for use in organic displays and sensors [1, 2]. Graphene and graphene materials, such as Graphene Oxide (GO), are promising for modifying the properties of conjugated polymers [3]. We studied the effect of graphene oxide on the structure and optical absorption of PoA nanocomposite films in the visible and near IR regions.

The FTIR spectrum of PoA film doped with GO demonstrated the new additional peaks at 2353, 2123 cm\(^{-1}\) (C=C); 1720 cm\(^{-1}\) (C=O); 1458 cm\(^{-1}\) (benzenoid rings), 1404 (C-OH); 1022 (C-O) and 650, 639 cm\(^{-1}\) confirm the insertion of GO nanosheets between PoA macromolecules. According to Transmission Electron Microscopy (TEM) data, the PoA film is characterized by an amorphous structure with a structural element size of 20–30 nm. Doping the film with GO changes the morphology of the nanolayer with the formation of individual sections of graphene sheets, and the size of the structural elements increases to 200–300 nm. In general, doping PoA with graphene oxide causes a change in the electronic structure of the conjugated polymer and significantly affects the morphology of the formed layer.

The absorption spectra of PoA films are characterized by three bands at \(E = 3.25 - 3\) eV due to the \(\pi \rightarrow \pi^*\) transition in the bandgap, at \(E = 2.1 - 2\) eV associated with the \(n \rightarrow \pi^*\) transition in the benzoquinoid system, and the absorption with a maximum of \(E = 1.5\) eV corresponds to delocalized charge carriers [4]. Doping does not affect the optical density and position of the absorption bands in the range of 2.5 - 4 eV for the PoA film with a thickness of 470 nm, while in the range of 1.25 - 2.5 eV PoA-GO film is more optically transparent compared to undoped PoA. In addition to the reduction of the absorption intensity, a shift towards lower energies is observed for the band caused by delocalized charge carriers during doping: from \(E = 1.7\) eV (for PoA) to \(E = 1.57\) eV (for PoA-GO).

Doping of PoA with graphene oxide causes a change in the optical absorption and structure of the polymer film. It can be assumed that the interaction of GO with the polymer reduces the energy of the electronic transition of charge carriers due to the ordering of the structure in the composite nanolayer PoA-GO.

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Physical & Chemical Water-sorption Processes in the MgAl$_2$O$_4$ Ceramics

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Processes of physical and chemical sorption of water occur in their internal and external defects and nanopores. This work studied water-sorption processes in the MgAl$_2$O$_4$ ceramics by Positron Annihilation Lifetime (PAL) spectroscopy.

The study of positron trapping defects caused by water molecules in adsorption/desorption cycles in MgAl$_2$O$_4$ ceramics sintered at 1400 °C for 2 hours was carried out in a specially designed humidity chamber at ambient temperature of 20 °C and Relative Humidity (RH) RH = 5% - 40% - 60% - 80% - 98% and RH = 40% - 60% - 80% - 98% - 80% - 60% - 40%. The processing of PAL spectra was carried out at fixed values of lifetime $t_1 = 0.17$ - 0.19 ns and $t_2 = 0.30$ - 0.39 ns depending on the background of the sample.

In the case of the experiment in adsorption-desorption cycles, the lifetime of the third component $t_3$ was fixed at the level of 1.9 ns. It should be noted that these results are in good agreement with data obtained without the use of a specially constructed camera to maintain a constant explosion. Within this approach, sorption influences are reflected in intensities $I_1$ and $I_2$.

It was shown [1] that positron annihilation processes in MgAl$_2$O$_4$ ceramics are adequately described by a multichannel model that combines positron trapping and ortho-positronium o-Ps decaying channels. The first component of the PAL spectra reflects the basic microstructural features of spinel ceramics. The second corresponds to defects localized near grain boundaries, and the third describes the “pick-off” annihilation of o-Ps in nanopores.

The intensity of the first component decreases with adsorption of water by nanopores of ceramics (RH = 40% - 60% - 80% - 98%) but increases at desorption (RH = 98% - 80% - 60% - 40%). The change in intensity of the second component will have an inverse character compared with the change of $I_1$. Thus, the intensity of $I_2$ increases with relative humidity RH changes from 40% to 98% and decreases when RH changes from 98% to 40%.

The intensity of the third component $I_3$ does not change and remains at the level of 1%. With such adsorption-desorption cycles in MgAl$_2$O$_4$ ceramics, this positron annihilation channel is insensitive to physically adsorbed water. Only in the so-called “forced” filling of the internal volume of nanopores with water this channel feels physically adsorbed water, which manifests in increasing intensity $I_3$.

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Preparation of Kaolin-Carbon-Orange Peel Powder Nanocomposites by Knife- or Planetary Ball-Milling

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Abstract ID #NSS- 0314

Kaolin, known as porcelain, Chinese clay or white clay, is a sedimentary rock that consists mainly of kaolinite, a natural layered mineral (aluminium silicate). The kaolin name originates from the hill in China (Kao-ling), where it has been mined for centuries. Kaolin is used in cosmetic recipes because of its nourishing, cleansing, and brightening properties [1].

Activated carbon, also known as a charcoal powder, or medical carbon, is an agent made of various materials of organic origin (wood, peat, fossil coal, or nutshells), is subjected to the process of carbonization at a high temperature, and is activated, which results in strong adsorption properties. Activated carbon is widely used in medicine as a remedy for food poisoning. Moreover, the activated carbon is more often appreciated in a cosmetic industry because of its whitening, cleansing, and even antibacterial attributes [2].

Orange peel is one of the ingredients useful in skin and hair care. It has a strong antioxidant effect, is rich in vitamin C, calcium, magnesium, and potassium. Orange peel powder is an effective exfoliating agent that helps in removing blackheads and unclogging pores. Orange peel powder lightens dark spots, and eliminates skin pigmentation [3].

A composite is a material that consists of two or more constituents that are characterized by a notably dissimilar chemical or physical properties and are combined to create a material with properties dissimilar to the individual components. Within the framework of finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions. A nanocomposite is a composite that at least one of the phases has one dimension lower than 100 nanometers. The combination of two or more ingredients in the form of the composite may provide an attractive cosmetic formulation with mixed characteristics [4, 5].

In this work, nanocomposites based on kaolin, activated carbon, and orange peel powder were obtained by mechanochemical activation using a knife- or ball-milling to ensure a high degree of phases dispersion. The effectiveness of phase binding was checked by FT-IR/ATR spectroscopy. The kinetic release of anthocyanin was determined using UV-Vis spectroscopy. Generally, results of the kinetic release of anthocyanin received by knife- or planetary ball-milling are comparable. The obtained materials may be used as cosmetic recipes.

REFERENCES

Effect of Hydrophilic Chain Topology on Aggregation of Amphiphilic Block Copolymers of Glicidol and Styrene

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In the last years amphiphilic block copolymers are widely studied for their use in controlled drug delivery systems [1, 2], carriers of biological markers [3] and many others. For the purpose of this work set of amphiphilic polystyrene-b-polyglycidol (PS-b-PGL), (PGL-b-PS-b-PGL) block copolymers and polystyrene-b-(polyglycidol-g-polyglycidol) (PS-b-(PGL-g-PGL)) coil-brush copolymers with similar molar mass and composition were prepared via anionic polymerization.

The self-assembly process of studied copolymers in water were investigated. The values of critical concentration of the copolymers’ self-assembly were measured. Critical concentration increases with increasing content of hydrophilic glycidol units in the copolymer chain. The size parameters of the aggregated structures were determined using DLS. Cryogenic transmission electron microscopy images revealed the presence of spherical objects, confirmed their sizes obtained with DLS and provided insight in their morphology.

ACKNOWLEDGMENTS

This work was supported by the National Science centre, project „Amphiphilic copolymers containing polystyrene/polyglycidol blocks with varied architecture and their functionalized derivatives – synthesis, properties, and aggregation, used as carriers of enzymes”, UMO-2018/29/B/ST4/02178.

REFERENCES

Composite of Polydimethylsiloxane (PDMS) and 2D Vanadium Carbide MXene(V$_2$CT$_x$) Films as a Flexible and Free-Standing Surface Enhanced Raman Scattering Substrate

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Abstract ID #NSS- 0338

Surface-enhanced Raman spectroscopy is a very sensitive technique that enables the molecular detection and identification of a wide range of analytes [1]. Flexible SERS substrates have gained great interest due to their easy handling and they are perfect for the real-time diagnosis of multiple analytes as compared to a rigid substrate [2]. On the other hand, two-dimensional (2D) carbide and nitrides (MXenes) have unique electrical and optical properties making them ideal 2D test materials for SERS study [3, 4]. Here, we have fabricated a transparent and flexible Polydimethylsiloxane (PDMS) and vanadium carbide (V$_2$CT$_x$) MXenes composite films for SERS application. We have demonstrated that a flexible composite film shows 4-8 times Raman enhancement for 10$^{-5}$ M methylene blue (MB) under different stretching and bending as compared to the initial state. The interaction between surface functional groups of MXene with dye molecules enhances the Raman signal making it a promising candidate for SERS application. This result encourages the making of flexible MXene-based SERS substrate as a wearable device.

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REFERENCES

Self-assembled Peptide Nanotubes of Different Chirality: Properties and Applications

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Abstract ID #NSS-0363

Chirality is a property of an object to be non-superimposable on its mirror image [1]. This simple, but the universal property of matter can be observed at various hierarchical levels from subatomic, molecular, and supramolecular to macro-and megascopic scales. An interest in chirality arises first from its ubiquitous presence in living matter. A huge number of chiral molecules such as amino acids (AA), sugars, etc. exist in nature and play a crucial role in living organisms.

Self-assembly of complex molecular structures based on AA is one of the most important phenomena both in living nature and in artificial biomimetics. At the same time, the chirality of the initial molecules also plays an important role in self-assembly processes. All this is important both for our understanding of wildlife and the basic principles of the emergence of life and for numerous practical applications. Self-organized macromolecules tend to form hierarchical structures with an alternation of the sign of chirality in the transition to a higher hierarchical level. Depending on the conformation of the primary structure (L or D), the properties of the material also change. An example of such self-assembled macromolecules is peptide nanotubes (PNTs) based on various amino acids and their dipeptides. Due to their wide-ranging physical properties, PNTs are not only important in the study of biomolecular self-organization, but also show promise in various applications in the nanotechnological and biomedical fields. One example of such self-organizing macromolecules is diphenylalanine (FF) peptide nanotubes.

In this work, we will discuss the experimental and theoretical study of the structure and growth kinetics of L-FF and D-FF microtubes. A better understanding of the role of chirality in the growth process will allow for improving the methods for nanotubes and microtubes fabrication, their better implementation in various functional devices, and may assist in the development of new drugs and biomaterials [2].

Moreover, the fabrication of layered biomolecular crystals of diphenylalanine obtained via a co-assembly of l,l- and d,d- enantiomers of FF monomers is also reported [3]. Their crystal structure, thermal and chemical stabilities, and piezoelectric properties are investigated. The grown crystals demonstrate better thermal and chemical stabilities than self-assembled hexagonal FF nanotubes. Piezoelectric bilayers, being held via weak aromatic interaction in the bulk crystals, can be exfoliated by mechanical or chemical methods, thus resulting in a 2D piezoelectric material, which can find various applications in biocompatible and ecologically friendly electromechanical microdevices, such as sensors, actuators, and energy harvesting elements used in implantable and wearable electronics.

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REFERENCES

Comparative Study of GNP-sprayed Carbon Fiber, GNP, and their Combination on the Mechanical Characteristics of Epoxy-based Multiscale Laminated Composite

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Abstract ID #NSS-0366

Carbon fiber reinforced polymer composites (CFRP) are gaining enormous research interest in the composites industry, particularly for automotive structural applications owing to their stiffness, strength, and low specific weight properties. In general, the in-plane properties of CFRP laminated composites are sufficient for many structural applications because of the high-performance fibers in the in-plane direction. In contrast, the through-thickness properties such as interlaminar shear strength (ILSS) are affected by matrix and fiber/matrix interface adhesion. The poor interface adhesion limits the applications of CFRP in many fields.

The modification of carbon fiber using the nanofiller could enhance the interfacial adhesion to the matrix and, ultimately, the mechanical properties. Further, introducing this modified carbon fiber in the nanofiller reinforced epoxy may improve the CFRPs composite’s mechanical performance. In connection to this, the present work compares the effects of GNP-sprayed carbon fiber (SGNP), GNP-reinforced epoxy (RGNP), and their combination (SRGNP) on the mechanical (tensile, fracture toughness, and ILSS) characteristics of carbon fiber multiscale laminated composites. The different compositions of GNPs (0.2, 0.5, 0.75, 1.0, and 1.25 wt. %) and the processing parameters for significant dispersion were optimized for spraying solution. It has been observed that 1 wt. % of GNP and 150 min probe sonication duration has shown to be optimal for spraying. The composite laminates were fabricated via the vacuum impregnation technique. The incorporation of 0.2 wt. % GNPs in epoxy and 1 wt. % spray GNP carbon fiber reinforced epoxy composites (SR GNP) enhance ultimate tensile strength by ~7.20 % over RGNP and ~38 % over SGNP, respectively, owing to significant adhesion between fiber and matrix. The fracture surface of the specimen was studied using a Field emission scanning electron microscope (FESEM) to evaluate the dispersion and distribution of GNPs in the nanocomposites and understand the strengthening/toughening mechanisms. Modulus mapping is carried out to understand the interfacial interaction between carbon fiber and reinforced epoxy, which influences the mechanical behavior of the multiscale composite. The obtained results indicate that the multiscale composite possesses enormous potential for structural application.

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REFERENCES

Characteristics of Nanostructures Formed during the Heat Treatment of Titanium (IV)isopropoxide Precipitates in the Presence of Noble Metals

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Abstract ID #NSS-0368

Titanium-based nanostructures were formed by the co-precipitation of titanium (IV) isopropoxide (TTIP) aqueous ethanol solutions with noble metal (NM) solutions in a weakly alkaline medium. It was found that regardless of the presence and nature of NM, only the anatase phase was identified by the XRD method in the powders obtained at T = 600 °C. The incorporation of NM into anatase structure was confirmed by varying the crystal lattice parameters and CSR. The increase in calcination temperature of the samples to 1000 °C shows that only the rutile phase was determined for the TiO₂&Pd system, while three polymorphic modifications of TiO₂ (anatase, rutile, and brookite) have been identified in pure TiO₂, TiO₂&Au, and TiO₂&Pt systems. The anatase phase was transformed into rutile in the TiO₂&Pd system (TG-DTA) at T = 780 °C, whereas the same reflex wasn’t detected in other studied systems. The average particle size of anatase was increased from ~30 to ~300 nm after the heating temperature increased from 600 to 1000 °C. The shape of anatase and rutile particles (tetragonal system) was close to the spherical type, but the brookite phase was represented by plates (hexagonal system).

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Preparation of Nitrogen-doped Graphene and Application as Catalyst for Fuel Cells

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Abstract ID #NSS- 0369

Graphene oxide (GO) has received remarkable attention as a valuable class of graphene derivatives, due to its chemical stability, high conductivity and ability to form chemical bonds easily. Doping with nitrogen could be an efficient way to modify the electrical, chemical, or physical properties of GO. Nitrogen-doped graphene (N/GO) has been extensively investigated as a promising catalyst for the oxygen reduction reaction, especially due to improved electronic properties in electron transfer reactions. This study presents an original approach: a fast and cost-effective method to prepare N/GO, starting from commercial graphene oxide, ammonia, and reducing agents; the reactions were carried out in a microwave field using various conditions. The obtained materials were characterized by different compositional, morphological, and structural characterization techniques and electrochemical methods.

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REFERENCES

Structural and Electrical Investigations of PEDOT:PSS Polymer Matrices Reinforced with Carbon Nanotubes

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Abstract ID #NSS-0392

Nanocomposites formed by the addition of nanosized filling elements into dielectric (often polymer) matrix are known to have extraordinary mechanical, thermal and electrical properties [1]. Among such nanocomposites of significant interest are PEDOT:PSS polymer matrices reinforced with carbon nanotubes which show great potential for sensor and other applications [2]. This particular polymer is one of the most studied and a lot of works have contributed to better understanding of PEDOT/PSS tailorable properties [3]. In this of work we experimentally analyze structural features and electrical behavior of PEDOT:PSS polymer layers with inclusions of high-purity single-walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) – two types of nanotubes that are characterized by high structural perfection.

Electrical studies were performed using E7-20 RLC measuring instrument. This instrument is designed to measure the parameters of samples represented by a parallel or serial two-element equivalent circuit. Harmonic voltage (1 V) in the frequency range from 1000 Hz up to 1 MHz was used as an excitation signal. The instrument ensures the 3% accuracy of impedance absolute value measurements. Based on the readings from E7-20 instrument, which initially measures absolute value of the impedance of the sample and phase angle between applied voltage and current through the sample, we have recalculated real and imaginary parts of the impedance.

All investigated samples show lowest impedance (highest conductivity) at room temperature and electrical conductivity decrease upon cooling. General trend is that Re(Z) slightly increases with frequency from 1 kHz to up to some threshold frequency and then drops rapidly. This threshold frequency for pure PEDOT:PSS and PEDOT:PSS/SWCNTs samples is about 100 kHz and is somewhat lower for composite layers with MWCNTs.

Most notable temperature effect on the real part of the impedance of fabricated polymer/CNTs composite layers is that Re (Z) increases drastically starting from certain temperature, which is different for samples with different composition. For pure polymer this occurs already at 80…90 K and below 60 K Re (Z) is almost out of the measurable range. For layers reinforced with SWCNTs, increase of impedance is more gradual and even more so for MWCNTs-reinforced composites. In the latter case, reliable measurements can be performed even at temperatures as low as 40K.

In samples with incorporated CNTs the conditions for residual water storage are potentially different due to structural changes introduced by specific nanofiller, so that time needed for complete water removal is different and the process is eventually finished at different temperature. This assumption is further supported by the fact that samples with MWCNTs show slower growth of real impedance with decreasing temperature and generally have higher conductivity at lowest measured temperatures.

REFERENCES

Fabrication of Various Photonic Systems Based on Self-assembled Nanospheres

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Abstract ID #NSS-0394

Monodisperse nanospheres of diameter of hundreds nanometers may serve for facile fabrication of 3D and 2D photonic crystals utilizing self-assembly phenomenon. 3D structures exhibit Bragg mirror reflection on crystal lattice and 2D – diffraction of light into colours. Opal-like and inverse opal structures may be obtained [1].

Self-assembly of nanospheres requires specific conditions, thus various techniques are used in order to find optimal conditions for fabrication of e. g. well-ordered 2D systems. Moreover, functionalization of nanospheres by luminescent dyes may require compatibility of the dye with the system, in order to control its concentration and to obtain it uniform distribution in the nanosphere volume.

Experimental results on fabrication of PMMA nanospheres of various diameter will be presented. The optical properties were dependent on their size. Several methods were tried for fabrication of 2D opals, e.g. Transfer from Air-Water Interface [2] and Confined Convective Assembly method [3].

2D inverse opals was fabricated on a top of waveguiding film for the purpose of coupling of light into the film. Ability of coupling of monochromatic and white light was investigated. The fabrication methods often lead to polydomain 2D opals, which show diversity of the spatial period of the structures along a chosen direction. This allows to obtain wider range of acceptance angle and/or wider spectrum of the coupled light.

In independent studies, we fabricated luminescent 3D opals by doping the nanospheres with organic luminescent dyes, selected to show high photoluminescence quantum efficiency. 3D opals with emission in different spectral range were fabricated. Dependence of emission spectrum and color versus the observation angle of the opals was determined. The materials with unusual angle-dependent emission color might find application in anti-counterfeight security features. Moreover, high quantum yield and uniform arrangement may allow for the use in photonic crystals lasers.

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REFERENCES

Phase Separations and Nematicity of Transition Metal Impurities

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Abstract ID #NSS-0397

Semiconductors [1] and topological materials [2] doped with transition metal elements attract considerable attention due to the fascinating physics and nonospintronic functionalities associated with exchange coupling between band carries and localized spins. However, there is a growing amount of evidence that d-shells of magnetic impurities contribute also to bonding, which can affect their spatial distribution and modify key properties, such as magnetic ordering temperature [3]. It has recently been experimentally demonstrated that the resulting phase separation (spinodal decomposition) can be anisotropic and result in the hitherto puzzling rotational symmetry breaking (i.e., nematic characteristics) revealed in a certain class of dilute magnetic semiconductors [4]. This finding put in a new light a possible origin of nematicity in other systems, such as unconventional superconductors and modulation doped semiconductor quantum wells, in which rotational symmetry breaking has so far been assigned to unidirectional spontaneous ordering of spin, orbital or charge degrees of freedom.

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*)

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Abstract ID #NSS- 0415

Progress in development of modern technologies forces the search for new materials that not only meet the application requirements, but are also environmentally friendly. As for functional materials in nano and micro-scale the size as well as shape plays very important role and influences the physico-chemical properties, it is crucial to synthesize materials with well-design morphology. Thus, in recent years there has been a growing interest in studies of ionic liquids (ILs). The physico-chemical properties of ILs as thermal stability, viscosity, density, melting temperature can be modified by selecting appropriate cations and anions. The extremely low vapor pressure and non-flammability of most ionic liquids makes them good candidates to replace some organic solvents and ILs are often called green solvents. It has been shown that ILs are very efficient media for nanoparticles synthesis, as they can act as in-situ stabilizer and the template for forming particles.

We already presented the using of ILs based method for the synthesis of luminescent efficient nanophosphors – fluorides and phosphates, and we are devolving this method to obtain highly luminescent and water-free materials of Nd³⁺/Yb³⁺-doped LnPO₄ and emitting in NIR spectral range.

Moreover, in our studies also we showed the application of ILs in photonic as materials, which could be used in lithography. Low vapour pressure makes ILs good candidates to use in vacuum techniques and consequently put a substrate with an ionic liquid layer into a chamber of Scanning Electron Microscope (SEM) equipped with Focused Ion Beam (FIB) source. Thin layer of this material can be obtained without using a solvent, which might be crucial in many technological processes.

Recently, we are focusing on using ILs in ionogels and in the thermochromic reactions, which bring a new opportunity of application of ionic liquids in multifunctional materials.

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Mixing Atoms in 2D Space or MXene Alloys of the Future

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Abstract ID #NSS- 0442

Discovery of new materials provides moments of inspiration and shifts in understanding, shaping the dynamic field of materials science. Following the graphene breakthrough, many other 2D materials emerged. Although many of them remain subjects of purely academic interest, others have jumped into the limelight due to their attractive properties, which have led to practical applications. Among the latter are 2D carbides and nitrides of transition metals known as MXenes [1]. The family of MXenes has been expanding rapidly since the discovery of Ti$_3$C$_2$ in 2011. More than 30 different stoichiometric MXenes have been reported, and the structure and properties of numerous other MXenes have been predicted. Moreover, the availability of solid solutions on M and X sites, multi-element high-entropy MXenes, control of surface terminations, and the discovery of out-of-plane ordered double-M o-MXenes (e.g., Mo$_2$TiC$_2$), as well as in-plane ordered i-MAX phases and their i-MXenes offer a potential for producing dozens of new distinct structures. However, most studies focus on Ti$_3$C$_2$Tx or a few other single-M MXenes, and little is known about the properties of solid-solution MXenes. Control of MXene properties via creating solid solutions of M and X sites and high-entropy alloys containing multiple M elements opens new horizons in materials science and engineering [2]. Using examples of niobium-based solid-solution MXenes (Ti$_{2-x}$Nb$_x$Tx and V$_{2-y}$Nb$_y$T$_x$; 0 ≤ y ≤ 2) we show the dependence of their electrochemical and physical properties on the ratio of M elements in the structure. Relationships between the chemistry and charge storage ability, conductivity and optical properties will be described. We have shown that physical, chemical and electrochemical properties of MXenes can be controlled by tuning the ratio of transition metals in the MXene structure.

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A MXene Modified Magnetic Alginate Hydrogels – An Application of Photothermal Effect in Enzymatic Catalysis

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Abstract ID #NSS- 0449

The light-to-heat conversion, known as a photothermal effect is based on the resonance response of the atoms under electromagnetic wave irradiation (light), where the heat is generated by movement or vibration of responsive atoms.

Inorganic semiconductor materials, carbon-based light absorbing materials, metallic nanostructures and polymeric materials are four main groups of light responsive photothermal materials. Among those, the transition metal carbides known as MXenes have demonstrated outstanding photothermal conversion by excellent electromagnetic wave absorption capacity as well as a localized surface plasmon resonance effect. Since their discovery, the vast majority of MXene-related applied research have been mainly focused on anticancer therapies and drug delivery systems.

In our work, the MXenes were applied as an active part of enzyme-based biocatalyst. The biocatalysts were formed by encapsulation of an enzyme (invertase) with magnetic iron oxide nanoparticles (Fe3O4/γ-Fe2O3) and the MXene flakes (Ti3C2Tx) in alginate hydrogel beads. Invertase catalyzes hydrolysis of sucrose to fructose and glucose, and the efficiency of catalytic reaction depend on sustaining the optimal temperature of the process. Therefore, using MXene photothermal effect, we were able to control the temperature and efficiency of the enzymatic reaction by controlling the power of external light source (808 nm).

The fabricated biocatalyst system offers the following advantages, namely: i) encapsulation of invertase in alginate beads allow to control the area of the enzymatic reaction and separation of enzyme from the substrate and products in reacting solution, ii) the presence of the magnetic core-shell nanoparticles grants possibility of “on/off” switch of the process, by removing the biocatalyst beads from reactor via magnetofection, and iii) presence of the MXenes allow to control the optimal temperature of the enzymatic process via laser irradiation of the hydrogel beads. All the nanomaterials were characterized by electron microscopies, IR and Raman spectroscopies, as well as powder X-ray diffraction. Four batches of biocatalysts were prepared by encapsulation of invertase, magnetic core-shell nanoparticles and MXene flakes in alginate beads: the invertase as a reference (I), the invertase with nanoparticles (II) or with MXenes (III), and with both of the materials (IV). Hydrogel biocatalysts were analyzed via cryo-scanning electron microscopy, while their dried xerogels by aforementioned characterization methods. The contactless energy conversion was studied by different external stimulations, namely: 808 nm laser, alternating magnetic field and dual. The biochemical analyses included estimation of protein concentration in biocatalysts and their enzymatic activity via estimation of glucose concentration in reactant solution.
Metal-support Interaction of Nanodiamonds and Palladium Nanoparticles in Cross-coupling Reactions

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Abstract ID #NSS-0457

Nanodiamonds (NDs) based catalysts are a significant class of nanomaterials with many possibilities of potential applications due to their unique structure, physicochemical properties dependent on nanomaterial composition [1, 2]. Nanodiamonds has been found as catalyst which has been applied as composite with or without metal support or modified with specific functional groups [3, 4]. Palladium nanoparticles (Pd NPs ~5 nm) supported on nanodiamonds (< 10 nm) were prepared by reduction of palladium (II) salt on oxidized nanodiamond. The synthesized catalyst was determined by XPS, XRD, AAS, TEM/HRTEM techniques including STEM-EDS chemical mapping revealed that the modified final material is combined of final reduced nanodiamond decorated with palladium nanoparticles. The well-characterized Pd@rNDs composite shows excellent catalytic activity especially for Suzuki-Miyaura cross-coupling reactions at ambient conditions, low temperature without any toxic solvents with good to high yields (>98%), excellent selectivity (>98%). The catalyst was also easily separated from the reaction mixture and reuse four times without loss of catalytic activity and chemical stability. The reaction was explored for the Suzuki reaction between 1-iodo-4-methylbenzene and phenylboronic acid as a model starting reaction; both non-metal NDs and Pd nanoparticles (Pd NPs) and even their mixtures showed no proceed reaction or results with substantially low conversions and selectivity. The versatility of nanocatalyst has been evaluated in various substrate range and reaction conditions. This environmentally friendly protocol facilitates easy possible use which may show new future exploration in heterogenous catalysis of C-C bond reactions.

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TRACK 2

“ELECTROCHEMISTRY OF NANOMATERIALS”
Stable Molecular-Organic Framework Based Electrode for Electrochemical Applications

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Prussian blue (PB) – a porous metal-organic framework has rendered its development in electrochromic devices, sensors, batteries and capacitors due to its unique electrochromic and electrocatalytic properties [1, 2]. For electrochromic devices, the presence of large interstitial voids and 3D ion diffusion pathways in PB allows facile accommodations of alkaline cations, thereby conferring PB an efficient color modulation material. However, the moderate ion-cycling stability of PB hinders its commercial development into practical devices because of its intrinsic structural imperfection and poor adhesion to the substrate. Numerous approaches have been developed to stabilize the intrinsic PB structure through the use of electrodeposition of PB in the electrolytic bath with sufficient K\textsuperscript{+} ions [3] and cyclic process in KCl bath [4]. Apart from adjusting the electrodeposition parameters, suitable interfacial engineering is also essential to improve the cycling stability. In this context, we demonstrate that PB-based electrode modified by polyaniline (PANI) demonstrates better cycling stability than the standalone PB electrode. By electro-depositing a layer of PB on the ITO substrate, followed by PANI deposition, a stable electrode with high charge density (~10 mC/cm\textsuperscript{2}) can be retained in KCl/DMSO chemical bath after cycling tests. Stable electrochemical properties and good morphological controls are demonstrated in the PB/PANI electrode using cyclic voltammetry and microscopic images, respectively. This work shows that a stable PB-based electrode for electrochemical devices can be achieved by reducing drastic volume expansion upon repeated charge-discharge cycling.

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Modification of Boron Doped Carbon Nanowalls by Electropolymerized Dopamine and Zwitterions – from Intermolecular Interactions to Enhanced Electrochemical Sensing

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Development of electrochemical biosensors is crucial for diagnosis and treatment of many diseases, where early detection of specified molecules is required. Examples of the increasing need for such devices include: detection of cancer biomarkers, neurotransmitters, hormones, continuous glucose monitoring and the whole spectrum of peptides and proteins [1]. For the rational design of sensing devices it is especially important to find the correspondence between the working principle of the sensor and the molecular sensing mechanism.

Connected with this paradigm, we report a functionalization of boron doped carbon nanowall (BCNW) electrodes with hybrid coating consisting of polydopamine (PDA) and polyzwitterions (PZ) for enhanced electrochemical sensing of neurotransmitters including dopamine, adrenaline and serotonin. Due to the high electrochemically active surface area and surface conductivity, BCNW substrates are potent platforms for sensing applications [2, 3].

First principles DFT calculations showed that zwitterions incorporated into PDA matrix facilitate transport of the analyte molecules towards the electrode through non-covalent intermolecular interactions. As a result, topology of the diffusion fields in the vicinity of BCNW electrode changes into microelectrode array, leading to enhanced amperometric response. Despite being the template for zwitterions, PDA exhibits catalytic effect for neurotransmitter electrooxidation governed by π-π and electrostatic interactions

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Nanocomposites Based on Polymeric Matrix With MXenes and Carbon Nanotubes as Nanofillers

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Abstract ID # EN - 0051

Polymeric nanocomposites represent a large class of materials, which possess numerous fascinating properties, improved due to combination of polymer matrix and various kinds of fillers [1]. Good interaction between matrix and filler provides enhanced characteristics, such as conductivity, toughness, capacitance, etc. Their continuous studies are broadening its fields of applications: nanoelectronics, medicine, energy generation and energy storage, as sensors [2] etc. Poly (methyl methacrylate) PMMA, which is a transparent, tough and lightweight thermoplastic due its characteristics, is mainly used as a glass substitute or as a cheap and not harmful alternative to polycarbonate.

MXenes, a big family of 2D nanomaterials, are highly studied nanoparticles [3]. They have metallic nature of the structure, strong bonds within its layers and adjustable group terminations [4]. Multi-walled carbon nanotubes (MWCNTs) are hollow multilayered cylinders, which are rolled single sheets of carbon covered with tubes of bigger diameter, because higher tensile strength, cheaper production they are used as nanofillers.

Composite samples were prepared using solvent casting method, where PMMA was dissolved in acetone. After adding fillers, MWCNTs and MXenes all was mixing on the magnetic and afterwards on mechanical stirrers.

Neat PMMA matrix, as most of the polymers, was not conductive (10^-14 S/cm). The quality of MXenes was tested with X-ray photoelectron spectroscopy (XPS), where no oxidation or extra amounts of residues from previous preparation steps were observed. Scanning electron microscopy (SEM) showed good results of delamination with obtaining 3-5 layer MXenes sheets, what is a good indication of getting close to single sheets. However, when PMMA/MXenes composites were tested, at 2.5 wt. % of filler load, the values were ~10^-4 S/cm, what indicates that there are quite enough of MXenes clusters, which form connections badly. PMMA/MWCNTs composites with only 0.5 wt. % showed 4 orders higher values, ~1 S/cm. In case of hybrid composites when only equally 1.0 wt. % of both fillers was used, the conductivity values reached 21 S/cm. It can be explained that MWCNTs are long flexible cylinders, which can easily disperse within the PMMA, and create additional connections between MXenes sheets.

Further study of these composites is testing for application as electromagnetic interference (EMI)-shielding coatings.

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REFERENCES

The Influence of Plasma-guided Phase Transformation on Optical, Structural and Photoelectrochemical Properties of Titania Nanotubes

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Abstract ID # EN - 0057

TiO$_2$ nanotubes have gained prominence in a variety of applications, from biomedicine, sensors, environmental analysis systems to energy storage devices or photocatalytic systems. This is possible due to their excellent biocompatibility, good tensile strength and corrosion resistance. One of the most applied methods to fabricate titania nanotubes is electrochemical anodization enabling precise control over the nanotubes geometrical features such as length or distance between them [1]. Nevertheless, such prepared nanotubes are amorphous and crystallization process is required to enhance their performance properties. Crystallization in the oven is well-known and well-described process, though it requires high temperatures and is time-consuming as taking into account the processing and cooling times it can last as long as 24 hours. Therefore, other routes for material crystallization are of high importance. Up to now low-temperature hydrothermal solid–gas route or laser treatment have been proposed but still their application is limited while the electrochemical and photoelectrochemical activities do not reach that observed for samples calcined in the oven. In here, we report plasma-induced TiO$_2$ nanotubes amorphous to anatase phase transition that overcomes that problem.

In order to induce plasma atmospheric pressure microwave microplasma source was used. The plasma was generated in nitrogen and power of 120 W was established. The microwave power was supplied through a 50 Ω coaxial line from a 2.45 GHz microwave magnetron generator and the microplasma was generated in the form of plasma jet above the inner conductor [2]. The distance (9-18 mm) between the sample and the inner conductor of the source was being changed to optimize the processing. The processing time was 30 s. SEM inspection of plasma-treated samples revealed that the nanostructured architecture of TiO$_2$ nanotubes was preserved. Raman and XRD measurements confirmed the successful crystallization of amorphous material. Photoelectrochemical results showed that for optimized conditions of plasma phase transition the obtained material can exhibit photocurrents 1.3 fold higher than those measured for TiO$_2$ nanotubes traditionally annealed in the oven.

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Mediated Electrochemistry of Cota Laccase from Bacillus Subtilis on Covalently-Functionalized Nanopatterned Surfaces for the Design of Oxygen-Reducing Biocathodes

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Abstract ID # EN - 0067

The integration of metal-containing enzymes into electrically-conducting nanomaterials is relevant for the development of bioelectronic devices such as sensors, diagnostic kits and biological fuel cells [1]. Nanopatterned materials are ideal because the specific immobilization of proteins onto nanometer scale areas ensures that their local concentration is very high, enhancing enzyme activity [2]. However, the functionalization of proteins on surfaces in defined positions and orientations with minimal loss in function and non-specific adsorption is challenging [3-4]. Here, the electrochemical characteristics of a nanopatterned biocathode based on the oriented and covalent immobilization of an extremophilic bacterial laccase CotA on nanopatterns is described. Using 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) redox-mediator, the immobilized CotA was shown to reduce oxygen, and achieved current densities of ~ 50 µA cm\(^{-2}\). Moreover, the site-selective immobilization of the enzyme in an oriented and covalent manner improved the current produced by ~ 60% compared to randomly adsorbed CotA. Finally, the system found to be more stable, maintaining 100% of CotA activity after 10 days, versus 25% of the initial activity when CotA is randomly adsorbed on nanopatterns.

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REFERENCES

Electrochemical Study of Quasicrystalline Al-Ni-Fe Alloys

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Al-based alloys produced by melt-spinning, water quenching, and copper mold casting are a promising group of advanced engineering materials. Rapid solidification techniques allow one to obtain quasicrystalline, amorphous, and nanocrystalline structures [1, 2]. Quasicrystalline materials have many favorable characteristics such as low thermal and electrical conductivity, low coefficient of friction along the aperiodic axes, mechanical strength, high hardness, thermal stability, and corrosion resistance [3]. The high resistance to corrosion at elevated temperatures makes quasicrystalline alloys promising construction materials in the aerospace sector [4].

The studied Al$_{71}$Ni$_{28}$Fe$_{1}$, Al$_{71}$Ni$_{24}$Fe$_{5}$, Al$_{71}$Ni$_{14.5}$Fe$_{14.5}$ alloys were proposed based on analysis of thermodynamic parameters. The samples for the investigations were prepared by induction melting (ingots) and high pressure casting into a copper mold (plates) [5]. The quasicrystalline phase D-Al$_{70.83}$Fe$_{9.83}$Ni$_{19.34}$ was identified in the Al$_{71}$Ni$_{24}$Fe$_{5}$ alloy in a form of plate. The alloy exhibits the highest Gibbs free energy of solid solution formation. The presence of a decagonal quasicrystalline phase was identified by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Mössbauer spectroscopy (MS) was used to describe the Fe local environment in crystalline and quasicrystalline alloys. Electrochemical measurements were made in a 3.5% NaCl solution at 25°C using a potentiostat equipped with a three-electrode cell. A saturated calomel electrode was used as the reference electrode, and a platinum rod was used as the counter electrode. The influence of quasicrystalline phases on improving corrosion resistance was investigated in a 3.5% NaCl solution. The presence of quasicrystals in Al$_{71}$Ni$_{24}$Fe$_{5}$ alloy gives it the highest corrosion resistance between proposed samples, as confirmed by electrochemical studies and observations by scanning electron microscopy.

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Corrosion Behavior of Al-Cr-Fe Alloys with Structurally Complex Phase Presence

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Abstract ID #EN-0104

The development of industry creates a demand for advanced lightweight materials [1]. Rapid solidification (RS) technologies make it possible to obtain unique structures and properties of aluminium alloys [2]. Special attention is paid to Al-based alloys with additions of transition metals (TM), such as chromium and iron, because of many favorable properties, such as improved corrosion resistance. In the latest work [3], a crystalline structure with the presence of a structurally complex alloy phase (SCAP) was identified by X-ray diffraction for Al-Cr-Fe alloys. The SCAP are intermetallic crystalline compounds that are characterized by large unit cells made up of thousands of atoms. Alloys with SCAP structure offer many interesting properties, such as high electrical conductivity at elevated temperature, low thermal conductivity, high hardness, low friction, and good corrosion resistance that could provide them with innovative applications in the future [4,5].

The purpose of the work was to characterize the structure and corrosion behavior of the Al₆₀Cr₂₀Fe₁₅ and Al₇₁Cr₂₄Fe₅ alloys produced by different cooling rates from the liquid state. The samples were produced by induction melting of chemical elements (99.99%) and then slowly cooling and high-pressure casting into a water-cooled copper mold. Structural studies were performed using X-ray diffraction, neutron diffraction, and scanning electron microscopy. The corrosion behavior was analyzed on the basis of electrochemical measurements carried out by the potentiodynamic method and electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl aqueous solution. The corrosion products were evaluated of the basis on X-ray photoelectron spectroscopy (XPS).

Al₆₀Cr₂₀Fe₁₅ and Al₇₁Cr₂₄Fe₅ alloys produced with two different cooling rates showed a crystalline structure with the presence of Al₆₀Cr₂₃Fe₈ that is structurally complex alloy phase. In the case of both chemical compositions, an improvement in corrosion resistance for high-pressure casted alloys was confirmed due to more positive values of corrosion potentials (Ecorr), higher values of polarization resistances (Rp), and lower values of corrosion current density (jcorr). Based on the Niqist plots the alloy Al₆₀Cr₂₀Fe₁₅ in a form of ingot and plate showed very good corrosion resistance. Based on the XPS results, it can be stated that the oxide layers consisting of Al₂O₃ for both compositions and Cr₂O₃ for Al₇₁Cr₂₄Fe₅ were formed. In the case of the Al₇₁Cr₂₄Fe₅ alloy, a higher intensity of the presence of oxides on the surface of the sample was recorded.

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REFERENCES

Modified Ultramicroelectrodes Arrays for applications in Environmental Analysis

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Abstract ID #EN- 0116

In this work, we report fabricated ultramicroelectrodes for environmental sensing platforms [1]. The three-electrode sensor chip was fabricated in a silicon wafer with 8 working electrodes with an HDMI-C connector that can be used for different applications. The microelectrodes have been modified for various applications including nitrate in the soil, dissolved oxygen, pH sensor, and heavy metal detection. With this platform, we can detect the analytes in the soil as well as in water sources [2]. The eight electrodes were modified with different with the aim of targeting different analytes, by just using one chip. Heavy metals detection is very important because of their toxicity, yet current methods are too complicated for point of care detection. Electrochemical sensors offer a convenient alternative for heavy metal determination, the sensor was tested for metals like lead using stripping voltammetry [3]. As lead is linked to several health effects and WHO identifies lead for 143,000 deaths annually the maximum allowable level of lead in drinking water is from 50 ppb to 10 ppb. Nitrate is one of the essential nutrients in the soil but because of overuse of fertilizers has made it important to detect the levels of nitrate in the soil. A varying nitrate concentration from 1 µM to 100 µM with a sensitivity of 0.038 A/µM with R² = 0.99 are investigated using differential pulse voltammetry. The fabricated sensor was also for dissolved oxygen and was studied to monitor the change of dissolved oxygen at different temperatures [4]. The final aim of the work is to develop an electronic reader with will allow portable sensing with readout measurement in smartphone applications [5]. The fabricated ultramicroelectrodes sensor with these electronics will provide a fully functional system for various environmental monitoring.

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Electrolyte-Centric Thermal Model of Li Ion Battery for Self-Powered Nanosystems

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Thermal management is of significant concern for Li-ion battery operation and storage. If the temperature surpasses certain limits, undesired exothermic chemical reactions may be triggered with a potential thermal runaway of the battery. This research analyzes the thermal behavior of an electrolyte-centric system with nano-scale dimension in the absence of passage of electric current. The model accounts for the Li ions, momentum, and thermal balance, considering free convection may occur within the electrolyte solution. Numerical calculations techniques are used for the study. The model concludes that heat can be dissipated properly in this type of system, avoiding thermal runaway outcomes. This is an important finding for energy storage applications where proper functioning is needed to guarantee continuous and independent operation, such as self-powered micro or nano electronic devices.

Self-powered electronic devices are gaining attention for fields such as health and environmental. Micro or nano scale gadgets are being used for a wide variety of applications such as medical implantable biosensors, nanorobotics, bio-chemical sensors for environmental applications, and even portable electronics [1, 2]. Li-ion batteries and capacitors are the preferred energy-storage devices for this kind of accomplishment. Safety is an essential concern in Li-ion battery operation and storage. One of the main concerns in these devices is the management of heat dissipation to avoid self-heating situations with potential thermal runaway outcomes. As temperature increases, secondary chemical reactions may be initiated, triggering an auto-catalytic feedback process (thermal runaway). This can potentially lead to complete degradation of the battery and possible explosion or combustion of the battery components. Several researchers have developed models to predict thermal behavior under conditions with potential thermal runaway outcomes on Li-ion batteries. Initial studies proposed a model that emulates the solid electrolyte interface (SEI) decomposition and regeneration reactions on a standard 18650 cylindrical cell [3]. Later works extended these models and included the reactions of cathode decomposition and electrolyte decomposition with potential combustion [4]. Although macroscopic level energy balance helps predict potential thermal behavior in a battery of multiple layers, the study of all the different transport mechanisms that happen inside a single-layer battery is essential for a better understanding of the process taking place when temperature begins to rise. With the aim of improving heat dissipation inside a battery, the electrolyte is a crucial component to consider as it can potentially handle heat flux easier through convection within the solution. According to our previous electrolyte-centric thermal runaway studies, hot spots can be localized at the interface between the negative electrode and the electrolyte solution [5].

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REFERENCES

Synthesis of Diamond-like Arsenolite Crystallites on Surface of Gallium Arsenide

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In this paper, we present results, describing oxidation method of a surface of the gallium arsenide. If semiconductor surfaces are naturally oxidized, inhomogeneity, amorphaousness and multicomponent of oxide coatings are observed \cite{1}. However, we have found that electrochemical etching of GaAs with subsequent electrochemical deposition, allows to form the diamond-like crystallites of the arsenic trioxide on the semiconductor surface in the cubic phase of the arsenolite. Such crystallites have the shape of regular dipyramids with triangular faces (tetrahedron). Morphological, chemical and structural characteristics of the formed layers were studied by SEM, EDX, Raman-spectroscopy methods. The spectrum of the composite light scattering shows the peaks from the gallium arsenide and arsenolite. No other connections were found on the surface. The peak shift of the Raman spectrum, which corresponds to the gallium arsenide, relative to the position of the typical peak for bulk-GaAs is explained by the presence of the porous layer on the GaAs surface. This layer was formed in the first etching stage.

The structural perfection of the arsenolite crystallites has been also studied. The crystallites have the shape of dipyramids with triangular faces. Some crystallites show twinning during the growth. It should be also noted that good crystallization and tight adhesion to the semiconductor substrate of the oxide layer is due to the chemical affinity of the materials (GaAs and As\textsubscript{2}O\textsubscript{3}), the similarity of the crystal parameters and the presence of the buffer porous layer.

Thus, the directed oxidation allows to create the passivating oxide layer that is uniform in volume and sample area. The complication of the natural oxidation of the surfaces of the nanostructured and bulk semiconductors is the multicomponent composition of the surface layers and the formation of different types of the native oxides simultaneously \cite{2}. The method of the directed controlled oxidation makes it possible to synthesize the oxide layer consisting of one type of the oxide, namely As\textsubscript{2}O\textsubscript{3}, in the cubic phase of the arsenolite.

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REFERENCES


Design and Characteristics of Doughnut-like Porous-CdO/Porous-CdS Nanostructures

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In this paper, we present the results of a simple synthesis method of the doughnut-like porous-CdO/porous-CdS nanostructures. The nanocomposite material was formed by the electrochemical etching method on the CdS surface simultaneously with the CdO electrochemical deposition by a two-stage route in the nitric acid solution. Electrochemical etching was used to form the porous-CdS layers as well as to saturate the electrolyte with the cadmium ions. Chemical deposition from the electrolyte solution was carried out with the CdO oxide crystallites on the surface. The obtained nanocomposite was characterized by SEM, EDX and Raman methods for the structural, morphological and component studies. According to the results of scanning electron microscopy, it was found that both the CdS surface and CdO oxide crystallites have a porous structure. Such high porosity (about 60%) and multifunctional advanced external morphology may be of interest for use in photovoltaic, catalytic and sensor devices. The structural characteristics studied by Raman and XRD spectroscopy showed that doughnut-like crystallites consist of the cubic phase cadmium oxide. Along with this there is a large number of amorphous CdO.

The similarity of the crystal lattices and structural parameters of the CdS and CdO allows to suggest that the CdS could be an excellent substrate for growing the CdO nanostructures.

Such structures are usually quite stable. Furthermore, the CdS porous structure serves as a soft substrate to avoid the tensions. In turn, the CdO layer is a reliable passivating layer for the CdS. Such coatings can often be characterized as conversion, i.e. protective. The oxide films reliably cover the semiconductor surface, thus serving as a passivating coating [1, 2].

The developed surface morphology of the obtained nanocomposite and the properties of its components (CdS, CdO) allow to consider it as a new material for photovoltaic devices. Furthermore, the increase in the surface area by hundreds of times and the unusual torus-shape of the crystallites can be used for photovoltaic energy converters, photocatalysts. The surface of CdS is susceptible to photocorrosion. To overcome this problem and improve the photocatalytic activity and stability of the surface layers, it is advisable to carry out the oxidation. In this way, it is possible to achieve the increase in the photocatalytic activity by the directed manipulation of the sizes, shape and crystallinity of the CdO nanostructures on the CdS surface.

The doughnut-like nanostructures are a new class of hybrid materials.

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REFERENCES


Highly Sensitive Chitosan/Carbon Based Electrochemical Sensor for Sunset Yellow Detection from Food Related Samples

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Synthetic colorants containing azo functional groups (-N=N-) and aromatic ring structures have been widely used to replace natural food colour in food industry due to the many advantages they offer: low production costs, excellent colour uniformity as well as high stability during preparation processes [1]. However, it is necessary to note that such synthetic colorants are able to affect human health being pathogenic, particularly when they are excessively consumed [2, 3]. Carbon-based materials are currently at the forefront of materials research due to their outstanding physical, mechanical and electrical properties and exceptional catalytic/electrocatalytic activity. The ability to be dispersed in various polymer matrix leads to a new class of polymer nanocomposites with a wide range of applicability (e.g. food packaging, biosensors, water treatment or drug delivery). The main goal of this study was to provide a facile, rapid, inexpensive way for the green, one-step and large-scale preparation of chitosan/carbon base nanomaterial, trough electrochemical exfoliation of graphite rods, without the use of any organic solvent [4]. The obtained nanocomposite was characterized from morphological and structural point of view. Moreover the applicability of chitosan/carbon based-glassy carbon modified electrodes for accurate detection and quantification of Sunset Yellow from commercially available food and beverage products was tested.

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Activation and Electrochemical Characterization of Poly(Lactic Acid) Based Composites with Carbon Nano-Fillers

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The 3D printed electrodes made of carbon black polylactic acid (CB-PLA) possess valuable electrochemical characteristics once their surface is activated properly. The aim of the activation process is to remove the polymer matrix and to reveal small particles of conductive carbon black filler. The most popular route of the activation is the immersion in dimethylformamide [1]. More environmentally friendly surface activation protocols include anodic and cathodic polarization in neutral electrolytes [2] or enzymatic activation using proteinase K [3]. Our recent studies focused on laser ablation treatment using pulsed laser, gave very good results in this regard [4]. Thus, the capability of a femtosecond laser ablation is now discussed, together with aspects of local, area-wise surface activation influence on the electrode electrochemical response. This electrodes have a big potential in sensing [1, 4] and energy-based application [5].

Commercially available conductive filaments for 3D printing contain in polymer matrix such fillers as: carbon nanotubes, carbon black or graphene. To improve 3D printing materials for electroanalytical application we decided to create our own materials. The carbon black is still main filler in PLA matrix but instead of it we add High Pressure High Temperature (HPHT) diamonds, Detonation Nanodiamond (DND) and Boron-doped-carbon Nanowalls (BCNW) on Glassy Carbon (GC) substrate.

Electrochemical analyses i.e. electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed to evaluate the kinetics of the charge transfer process after local surface activation and new 3D printing conductive materials. Additionally the impedance spectroscopy for created materials was perform to check the additives change the conductivity. The results shows that the laser ablation process is a high-efficiency method for electro-activation of CB-PLA surface. Also the additives like DND, HPHT diamonds and BCNW on GC improve the electrochemical activity of created electrodes.

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Conference Track: “Electrochemistry of Nanomaterials”
Jewelry or Science: Impedimetric Monitoring of Molecular Recognition Systems Based on Diamond and Gold Surfaces

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Abstract ID #EN-0212

Nowadays, electroanalytical laboratories resemble jewelry stores full of diamond-based and noble metal (Au, Pt) electrodes. This is because of their electrocatalytic properties, enhancement of the electron transfer process, extraordinary affinity to certain compounds allowing reproducible grafting routes, as well as high corrosion resistance and stability. Furthermore, constantly striving for higher limits of detection or antifouling properties, these substrates may be tailored for desirable performance. As a result, different derivatives of these noble materials are commonly found in many electrochemical sensors.

Reaching the desirable performance on complex electrode substrates introduces significant reproducibility issues, scaling-up and cost-efficiency, and others. For example, boron-doped diamond (BDD) is particularly intriguing considering major morphological factors affecting electric heterogeneities detrimental to the electrochemical performance, such as $sp^2$/$sp^3$-carbon phase composition, crystal lattice texture, distribution of boron dopant, and electrode termination type. On the other hand, gold and other noble metal nanoparticles struggle from low stability and low coverage uniformity dependent on the synthesis and deposition route and passivation by surfactants. The global electrode behavior is further influenced by functionalization layer homogeneity and thickness, stability, etc.

Impedance analysis techniques are among the most promising tools used in electrochemical biosensors. The most commonly used identification approach is the variation of charge transfer resistance upon specific analyte adsorption at an appropriately functionalized electrode surface. However, the detection may also base on other factors, such as raw impedance, adsorption layer capacitance, or even disturbance in frequency dispersion of capacitance. Recently, multisinusoidal monitoring with Dynamic Electrochemical Impedance Spectroscopy (DEIS) was proposed by our group for simultaneous tracking of the impedimetric characteristic upon alteration of the polarization conditions. As a result, we obtain the unique fingerprint of the electric parameter changes, dependent on macromolecular charge, size, hydrophilicity, and others. Our approach, combining potentiodynamic DEIS measurement with extended statistical studies, was used for human-specific DEF-B1 aptasensor from saliva and, more recently, allowed us to study and detect subtle changes in the electric properties responsible for the susceptibility of various cellular receptors to SARS-CoV-2. The proposed approach neglects some of the reproducibility issues induced by non-specific adsorption and fouling and reveals the measurement conditions that offer the highest variation of studied parameters upon specific analyte adsorption. In this talk, some of the principal problems of biosensing at heterogeneous electrodes will be discussed, with the routes to overcome them with classic impedance measurements or DEIS.

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Influence of Short-Term Annealing on Electrochemical Properties of Amorphous Metal Alloys Based on Aluminum

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Abstract ID #EN-0216

Aluminum metallic amorphous alloys (AMA) are interested because of a good corrosion resistance, a low price of aluminum, which is important in production of construction materials and electrodes. The intensive development of alternative energy sources, in particular chemical power sources, requires the search for new electrode materials that provide high specific energy [1–2]. Temperatures of annealing of AMAs were determined by differential scanning calorimetry (DSC) phase transitions of amorphous metal alloys (AMA) of the Al – Ni – Y (Gd) system. Annealing at T3 leads to the formation of an amorphous matrix intermetallic compounds causes a shift in the corrosion potential in the cathode direction and there is growth corrosion currents density, respectively, the resistance at the electrode/solution boundary drops sharply. Double electric layer processes at the AMA/aqueous solution of 0.3% NaCl and the effect of Y and/or Gd on the corrosion resistance of the initial and annealed samples were investigated. The influence of the structural state and nature of alloying additions on the corrosion characteristics of aluminum electrodes were determined.

REFERENCES
Corrosion Properties of \([(\text{Cu-Zn}_1)/(\text{Cu-Zn}_2)]_n\)
Nanostructured Multilayer Coatings

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Abstract ID #EN- 0251

Multilayer coatings, consisting of periodically alternating layers of alloys of different composition with thickness of up to 100 nm, were designed to improve the properties of classic single-layer galvanic coatings. For example, Cu-Zn alloys are used as coatings to increase protection against aggressive media, to protect steel from corrosion, as well as catalytically active electrode material, and as shape memory alloy films in microelectromechanical systems and other micro-dimensional applications [1-3]. Therefore, it is important to study the corrosion properties of multilayer coatings \([(\text{Cu-Zn}_1)/(\text{Cu-Zn}_2)]_n\).

The aim of the study is to identify the influence of electrodeposition conditions of multilayer coatings on their corrosion properties. Multilayer \([(\text{Cu-Zn}_1)/(\text{Cu-Zn}_2)]_n\) coatings were deposited by a two-pulse galvanostatic method from a polyligand pyrophosphate-citrate electrolyte. The method allows to obtain compact thin films of copper-zinc alloy of different elemental and phase composition. The values of polarization resistance, corrosion potentials and corrosion currents of coatings are determined for multilayer coatings of different total thickness, consisting of films of alloys of different composition and thickness. The values are compared with single-layer coatings by alloys obtained in the conditions of deposition of constituent layers of multilayer coatings.

REFERENCES

Natural Solvent-based High Shear Exfoliated Few Layered Graphene for Non-enzymatic Electrochemical Sensing of H$_2$O$_2$

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Abstract ID # EN-0280

Graphene-based nanomaterials are one of the best electrode materials for electrochemical sensing applications due to their excellent electrocatalytic activity, stability over a wide potential window, good conductivity, and high surface area. The ever-increasing need for graphene-based nanomaterials requires an efficient production method. This study explains the potential usage of high shear exfoliated few-layered graphene (HSE-FLG) in electrochemical sensing applications. FLG was prepared in bulk by using a low-cost and eco-friendly high-shear liquid-phase exfoliation method in an aqueous (water) medium by using minimal amounts of organic additives. The standard electrochemical characterizations of prepared HSE-FLG modified GCE showed excellent electrocatalytic activity due to the increased electrochemically active surface. The potential usage of prepared HSE-FLG in electrochemical sensing applications was confirmed by non-enzymatic amperometric sensing of H$_2$O$_2$. The prepared sensors have shown significant improvement in terms of sensitivity compared to recently published H$_2$O$_2$ sensors.

REFERENCES


Modeling the Composition of the Pre-Cathode Layer in Dicyanoargentate Buffer Electrolyte without Excess Ligand

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Abstract ID #EN- 0281

Silvering electrolytes, which are mostly used in practice are based on KAg(CN)₂ with a significant excess of free ligand, injected into the solution as cyanic salts of alkaline metals [1]. The study of the silvering mechanism is also usually carried out using electrolytes containing an excess of cyanide ions, which simplifies the investigation [2]. As was shown in [3], the study of the mechanism and kinetics of metals electrodeposition from complex compounds with a small excess of ligand or especially containing no additional amount of ligand in the initial moment has some particularities. In this case, the composition of the pre-electrodic layer is much different from the composition of the bulk of the solution.

We developed a BPC electrolyte based on the K[Ag(CN)₂] complex and a high-capacity borate-phosphate-carbonate buffer [4]. This electrolyte is one of the most promising ones for the replacement of cyanide electrolytes for functional silver plating. High-quality functional-silver deposits are obtained from the BPC electrolyte, which is preferable to coatings deposited from other known silver-plating electrolytes having many physicochemical and mechanical characteristics [5].

Therefore, to determine the mechanism and kinetics of electrochemical reduction of silver from the electrolyte containing KAg(CN)₂ and BPC buffer and to choose an optimal composition of the electrolyte, the information about ionic composition both of the solution bulk and at the surface of the electrode (in a pre-cathodic layer) is important. In addition, this information allows us to solve the problem of replacing highly toxic cyanide electrolytes with the most perspective electrolytes based on the borate-phosphate-carbonate buffer to obtain functional coatings in electrotechnique for manufacturing of micro-, and nanoelectronic devices.

The pre-cathode layer composition during silver electrodeposition in borate-phosphate-carbonate (BPC) buffered electrolyte on the base of dicyanoargentate complex had been modeled. The mass-transfer processes in BPC silvering electrolytes without the excess of the ligand had been investigated. The investigated borate-phosphate-carbonate buffering system operates at pH 7.0, and the ionic composition of the electrolyte was calculated exactly for these conditions. Concentrations of ions in the electrolyte bulk are calculated, as well as the dependence of pre-cathodic layer composition on the current density. The kinetic of silver electrodeposition from borate-phosphate-carbonate solutions containing KAg(CN)₂ and BPC buffer has mixed character.

REFERENCES
Semiconductor Properties of Surface Layers of Nanostructured Aluminum-based Alloys

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Abstract ID #EN- 0289

The high corrosion resistance of amorphous aluminum-based alloys in aggressive environments is due to passivating layers, which are less defective due to the uniform distribution in the amorphous aluminum matrix of alloying additives of rare earth and transition metals [1, 2]. The work aims to study the influence of nanostructuring of amorphous aluminum-based alloys on the nature of protective oxide-hydroxide layers. It is known that isothermal annealing leads to nanocrystallization of AMA Al$_87$RE$_5$TM$_8$ (RE = Y, Dy, Gd, TM = Ni, Fe). Annealing affects not only the bulk structure of AMA but also the semiconductor properties of the surface layers. Electrochemical methods (voltammetry, electrochemical impedance spectroscopy (EIS)) have shown that aluminum nanocrystals change the corrosion resistance of AMA in 0.3% aqueous NaCl solution. It is shown that the nature of the formed oxide layers on the surface of AMA Al$_87$RE$_5$TM$_8$ before and after their annealing was investigated by EIS and analyzed by Mott-Schottky dependencies. It is established that the nanostructuring of AMA leads to a change in the conductivity of oxide layers from n-type to p-type. AMA Al$_87$Y$_4$Dy$_1$Ni$_8$, annealed at 611 K, leads to the formation of surface protective layers of p-conductivity with a charge carrier density of $10^{18}$ - $10^{19}$ charges / cm$^3$. The value of the flat-band potential is $-(1.11 - 1.12)$ V, which does not depend on the annealing of the samples.

ACKNOWLEDGMENTS

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Electrochemical Fabrication of L-HIS-MWCNTS@PDMS/MIP Sensor for Sensitive Tetracycline Detection

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Abstract ID #EN- 0302

Electrochemical methods are considered promising for the sensing of contaminants due to their simple instrumentation, fast analysis, low cost, and high sensitivity [1]. It is well known that molecularly imprinted polymers (MIP) are a powerful technique for designing biomimetic materials capable of recognizing target molecules with special selectivity [2]. Some MIP-based electrochemical sensors have been developed to combine the advantages of MIP and electrochemical techniques. Molecularly imprinted electrochemical sensors (MIECS) due to their recognition properties, low cost, and the possibility of easy automation make them an ideal candidate for the detection of a variety of pharmaceuticals. Nanomaterials, such as multi-walled carbon nanotubes (MWCNTs), have many advantages, like large surface area, electrical conductivity, thermal and chemical stability, economic effectiveness, and electrocatalytic activity [3], and have offered alternative approaches for sensitive and low-cost detection of tetracycline (TET) in various media. Moreover, carbon nanotubes can also be used in sensors after mixing them with a polymer matrix to form MWCNTs composites. Poly(dimethylsiloxane) (PDMS) elastomer is the most commonly used in diagnostic tools due to its chemical stability, physiological indifference, simple fabrication, and biocompatibility [4].

For the first time, we report the fabrication of a new hybrid electrochemical sensor based on molecularly imprint containing L-histidine-MWCNTs@PDMS (L-His-MWCNTs@PDMS/MIP) for selective, fast, and simple sensing of TET. The polymer nanocomposite (MWCNTs@PDMS-5) is prepared by physical adsorption of PDMS-1000 liquid (Mw ≈ 7960) onto pristine multi-walled carbon nanotubes (P-MWCNTs) in the amount of 5 wt. %. The surface properties of P-MWCNTs and prepared MWCNTs@PDMS nanocomposite were characterized with FTIR-ATR, Raman spectroscopy, XRD, SEM, and particle size distribution (PSD) techniques. The PSDs for P-MWCNTs and MWCNTs@PDMS-5 samples are similar and show a bimodal size distribution. SEM images for both of them demonstrate the presence of carbon nanotubes bundles and catalyst residues. It was found that the external diameter of the P-MWCNTs is approximately 30–50 nm. At the same time, the electrochemical performances of the developed sensors were evaluated using the methods of differential pulse voltammetry (DPV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). This sensor has been achieved with high sensitivity, very low limit of LOD (2.642 x 10^-12 M), and LOQ (8.807 x 10^-12 M) values, with non-toxic solvents and minimal waste generation. The validity of the sensor was checked by TET detection in capsule dosage form, human serum, and tap water samples, and the recovery results were found to be 99.69 %, 98.92 %, and 100.60 %, respectively. The created L-His-MWCNTs@PDMS/MIP sensor offers the benefits of TET detection and can be reliably applied to real samples.

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Easy, One-pot Preparation of the NiCu-Graphene Oxide Catalyst Using Electrodeposition and Its Activity Towards Electrooxidation of Urea

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Abstract ID #EN-0310

Due to the increasing world population and the growth of civilization, energy demand will continue to grow. Considering the political tensions related to fossil fuel mining and the increasing climate crisis, it becomes clear that new energy sources are necessary. Among them are fuel cells – devices capable of direct conversion of the substrates’ chemical energy into electricity during a redox reaction. They have received a lot of attention because substances that be used as fuels, like simple alcohols or urea, are much more environmentally friendly than fossil fuels. Especially urea deserves our attention, due to its large amounts present in the wastewaters, which are now considered a waste but could potentially be used as a fuel.

One of the main challenges that need to be faced with making fuel cells commercially available is the lack of electrode materials that would be cheap, reactive, and durable at the same time. To overcome this obstacle, we show an easy, one-pot method of electrocatalytic composite preparation. Using a well-developed electrodeposition process, we prepared a material consisting of nickel, copper, and graphene oxide (GO) and proved its activity toward urea oxidation reaction (UOR).

We found that cathodic polarization in a proper solution, containing both Ni and Cu salts with the addition of GO, leads to the formation of coral-like composite particles with higher surface area and higher electrocatalytic activity towards UOR, proven by cyclic voltammetry (CV) than NiCu particles prepared using the same method. To further examine the mechanism of UOR, we conducted bulk electrolysis of urea with an analysis of the reaction products using high-pressure ion chromatography (HPIC) and high-pressure liquid chromatography (HPLC). We found that the clamping voltage required for reconstruction of current densities observed during CV scans has been lower for our composite than for pure nickel. Analysis of the urea concentration, identified using HPLC, has shown that NiCuGO is reduced the urea concentration more strongly than Ni for the same reaction conditions. However, analysis with HPIC has shown that solutions oxidized using NiCuGO content of NO$_2^-$ ions is higher than for the solutions oxidized using Ni as an anodic material.

Detection of NO$_2^-$ ions means that urea got overoxidized, which was also reported by other scientists, like Li et al. [1]. The presence of this type of UOR by-products in the wastewaters is a big threat to the environment, so further research is needed for UOR optimization, leading to more environmentally friendly products, like NO$_2$. It also shows that the widely agreed mechanism of urea oxidation on Ni-based catalysts leading to N$_2$, CO$_2$, and H$_2$O is not accurate in some cases and that product analysis is crucial for the catalyst reactivity assessment.

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Unveiling the Role of Cu in Carrier Transport and Dielectric Relaxation Using Impedance and Modulus Spectroscopy in TiO₂ Thin Film Electrodes

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Abstract ID #EN-0343

TiO₂ is the supreme candidate among the wide bandgap metal oxide semiconductors for energy applications [1-3] due to its miraculous properties. It is crucial to build a fundamental understanding of charge transport and different dielectric relaxation processes in the material to increase the efficiency of the TiO₂ electrodes for energy and photovoltaic applications. The critical issue with pristine TiO₂ in photocatalysis and photo-electrocatalysis is low photo efficiency due to its wide bandgap structure. We fabricated the TiO₂ based thin film electrodes via spin coating method. To improve the photo efficiency of the electrodes, we doped TiO₂ with Cu. We found a significant increment in the visible light absorption with Cu doping. To improve the electro-catalytic and photocatalytic efficiency, we must ensure that many charge carriers reach the surface before recombination.

Consequently, we performed Electrochemical Impedance Spectroscopy (EIS) and Modulus spectroscopy to study the charge carrier kinetics and dielectric relaxation process of pristine and Cu doped TiO₂ electrodes over the frequency range 0.1 Hz to 1 MHz. After Cu doping in TiO₂, we observed the frequency dependence of electric permittivity over an extensive frequency range (0.1 Hz to 1 kHz) diminishes astonishingly. Furthermore, correlating the impedance and modulus spectra manifests the localized charge carrier relaxation in Cu doped TiO₂, from which we developed an exceptional understanding of the hopping process of charge carriers.

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REFERENCES

Anabaena sp. Immobilized RGO-PPY Nanocomposite Based Photoanode for Bio-Electricity Generation in Non-Mediated Bio Photovoltaic Cell

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Abstract ID #EN-0359

There is utmost requirement of exploration of suitable electrode nanomaterial having excellent conductivity, high specific surface area, good biocompatibility, and chemical stability for potential application in Bio-photovoltaic devices. Novel or modified 2D electrode nanomaterial with inherent conductive properties may enable fabrication of high-performance bio photovoltaic cells in context of net power output. The applicability of graphene and its nanocomposite with conductive polymer in BPVs offers promising results than conventional ITO and carbon based electrode materials due to enhanced conductivity and high surface area which also enables effective adsorption of cyanobacteria, exhibiting augmented power production and durability. Therefore, the present work focuses on the synthesis of an efficient rGO-PPy nanocomposite based photoanode for bio electricity production using a cyanobacterium called Anabaena sp. in bio photovoltaic cell. The immobilization of Anabaena sp. (NOS) on synthesized photoanode material with high electrochemical activity and stability facilitates enhanced power output in electrochemical fuel cell set up which further lays foundation for construction of cost-efficient and high-performance BPVs.

REFERENCES

Development of Inexpensive, High Performance Carbon Supported Catalyst Nanomaterials for Iron-free Fenton-like Catalytic Water Treatment

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Abstract
Globally 1 in 3 people don’t have access to safe drinking water [1]. The presence of micropollutants is an important contributor to this, as current industrial treatment methods cannot effectively remove them due to their chemical stability and very low concentration. These persistent pollutants include pharmaceuticals, steroid hormones, surfactants, industrial chemicals and pesticides, and can have significant adverse health effects, even causing endocrine disruptions [2].

Most large scale water purification methods are based on adsorption, not degradation, but even current degradation methods come with significant drawbacks; Most importantly high installation and operation costs, and production of a toxic sludge in Fe-based homogeneous Fenton systems [3].

This work aims to synthesise carbon supported Co, Mn spinels to produce high performance catalyst materials for heterogeneous Fenton-like chemistry-based water treatment systems that outperform current state of the art catalysts using inexpensive materials and synthetic methods. Catalytic activity is investigated for materials of different Co:Mn and spinel: support ratios to elucidate structure-performance relationships.

The catalytic activities of these materials were tested in dye degradation reactions which serve as a model for the removal of persistent organics from real effluents. There is a remarkable difference in performance based on the symmetries of sites metal ions occupy. Composite formation method also has an outsized effect on catalytic activity, which supports the hypothesis that high aspect ratio supports are more suitable as catalyst supports.

Further development and scale-up of this system could open the door to the commercialisation of this method and thus contribute to keeping water supplies drinkable long term.

REFERENCES
Synthesis, Characterization and Energy Transfer Mechanism Analysis of Nd$^{3+}$; Yb$^{3+}$-co-Doped YPO$_4$ Nano and Micro-Crystalline Powders

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Abstract ID #EN- 0419

At the turn of the last few decades, due to rapid technological development, scientists have particularly focused on compounds doped with RE$^{3+}$ ions, that showed efficient laser properties. Recently, research on high-performance diode-pumped solid-state lasers has promoted the preparation of Yb$^{3+}$-doped materials such as vanadates [1] and tungstates [2], co-doped with other various lanthanides ions. Among these ions, neodymium ion Nd$^{3+}$ is one of the most efficient RE for doping in different host matrix [3].

In this study we present the preparation and analysis of structural and spectroscopic properties of Nd$^{3+}$; Yb$^{3+}$-co-doped YPO$_4$ nano/micro-materials, obtained by various methods of synthesis – microwave-assisted hydrothermal method and solid-state synthesis. Materials with different concentrations of activators were used in order to examine possible changes in structural and spectroscopic properties and study quantum cutting phenomenon between Nd$^{3+}$ and Yb$^{3+}$ ions.

XRD technique confirmed that obtained YPO$_4$ powders crystallize in tetragonal system (I41/amd) and their phase purity. Electron microscopy, SEM and TEM, was used to demonstrate the differences in the morphology and size of micro/nano-materials, which brings the consequences in the spectroscopic properties. The spectroscopic properties and possible energy transfer were analyzed by using low-temperature high-resolution techniques like absorption spectroscopy at 4.2 K and tunable laser site-selective spectroscopy at 77 K. The strong multi-wavelength emission of Yb$^{3+}$ and Nd$^{3+}$ ions was successfully achieved simultaneously for both, nano and micro-materials. Energy transfer mechanism between these ions was proposed for studied host matrix.

REFERENCES


Single Step Fabrication of Tungsten Nitride Based Symmetric Supercapacitor

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Abstract ID #EN- 0428

Transition metal nitrides-based thin-film supercapacitors are attracting researchers around the globe owing to their high-class electrochemical performances, good sustainability, and considerable voltage window. The present work presents the single-step fabrication of tungsten nitride (WN) on a stainless steel-304A (SS) wafer for highly efficient symmetric supercapacitor (SC) applications. The reactive sputtering technique is used to deposit the metal nitrides in argon and nitrogen (Ar/N\textsubscript{2}) environment. The SC is fabricated using WN@SS as the working electrode. All the electrochemical studies are performed in aqueous electrolyte at different current densities and scan rates. The structural, morphological, and crystallographic characterizations of the electrode are also performed. The WN@SS electrode-based symmetric supercapacitor demonstrated in this work show exceptional electrochemical stability and capacitive performance, broader voltage window, good adhesion, and excellent cycle life. Owing to these interesting properties, the proposed SC can be considered as a promising candidate toward the fabrication of energy storage devices.
TRACK 3

“MULTIFUNCTIONAL THIN FILMS & COATINGS”
Controlling Interfacial Interactions and Orientations of Amphiphilic Tetraazaporphyrins by Molecular Design

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Abstract ID #MTFC-0007

The orientation of dyes at interfaces significantly affects their electronic and optical interactions with another material and the overall properties of a coating. Particularly large differences in electronic coupling and absorption and emission properties are expected between monolayers of porphyrinoids with edge-on and flat-on orientations. While an edge-on orientation is straightforward to achieve with appropriately substituted porphyrinoids because of their strong co-facial interactions, these same interactions often disfavor a flat-on orientation of these dyes.

Reported here are the synthesis and Langmuir-Blodgett (LB) properties of amphiphilic tetraazaporphyrins (TAPs) with one alkyl chain and one carboxylic acid terminated aliphatic chain at each of their four pyrrole groups. This arrangement of carboxylic acid groups is expected to pin down the TAP macrocycle onto a polar surface while the aliphatic chains are expected to fill the space above the macrocycle (away from the interface) to generate an overall amphiphilic rod-like structure. In contrast, amphiphilic compounds give edge-on orientations and were prepared and studied as reference compounds. For their synthesis, the established pathway starting with the alkylation of maleonitriledithiolate followed by the templated cyclization in magnesium propanolate was chosen. Efficiently alkylation of maleonitriledithiolates with two different alkyl groups was achieved by flow chemistry. Langmuir studies were performed on the metal-free and nickel metallated derivatives at different pH values of the aqueous subphase to control self-aggregation and amphiphilicity of the TAPs. The most stable Langmuir and LB films with a flat-on orientation of the TAP macrocycle were obtained for TAPs with branched alkyl chains. This is reasoned with their ability to fill the space above each TAP ring most effectively.
Nanocolumnar Films by Magnetron Sputtering: Fundamentals and Applications in Medicine, Energy and Aerospace Industry

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Abstract ID #MTFC-0040

In this talk, I will briefly show that nanocolumnar films can be manufactured by magnetron sputtering using the glancing angle deposition configuration. This technique is environmentally friendly, since it is carried out at room temperature in a single step and does not involve chemical products (i.e. no recycling issues). Depending on several parameters (mainly the gas pressure, the angle of inclination of the substrate and its possible rotation), the nanocolumnar structure can be controlled. Furthermore, this method can be scaled up to large surfaces, representing a valid approach for the industrial production of nanostructured films [1]. Then, in the second part of the talk, I will show several applications of these nanocolumnar films in medicine, energy & environment and the aerospace industry, such as antibacterial coatings for orthopedic implants [1], bioelectrodes for an electric stimulation platform in vitro [2], nanostructured layer for advanced perovskite solar cells [3], magnetic nanopillars [4], and anti-multipactor coatings for the space industry [5], among others.

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The Influence of the Geometry of the Alkyl Group on the Properties of Diketopyrrolopyrrole in Solution and Langmuir Thin Film

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Abstract ID #MTFC-0091

Diketopyrrolopyrrole (DPP) are organic semiconducting dyes which main building block is bicyclic dilactam that can be modified by attaching external groups to lactam nitrogens and carbon atoms [1]. DPPs are well known for their high stability, low solubility, intensive absorption in the visible spectrum, and high charge-carrier mobility. DPP's derivatives can act as p-type, n-type, or ambipolar semiconductors [2]. Changes in chemical structure can affect DPPs solubility in organic solvents, their optoelectronic properties, and as a result efficiency of the photovoltaic device [3-5]. Although it is known that the replacement of lactam nitrogen with an alkyl group leads to an increase in solubility [2] the influence of its geometry on other properties in form of Langmuir layers was not studied yet. For this purpose subjected to research were two DPP dyes containing symmetrically attached terthiophenes that ended with an alkyl chain (C6H13) differing in the geometry of the alkyl group (straight and branched chain) tied to amide groups. Spectroscopic and electrochemical studies, performed to obtain information about energy gap, HOMO, and LUMO energy levels, were made for materials in solutions in organic solvents and thin films. Thin films of DPPs created on the air-water interface by the Langmuir technique were transferred onto the solid substrate using Langmuir-Blodgett and Langmuir-Schaefer method. During the compression of Langmuir layers, various experimental techniques were used to obtain information about the mutual orientation of dyes molecules and changes in optical properties. Density functional theory (DFT) calculations were carried out with the aim to compare theoretical and experimental results.

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Electron Beam Modification of Hybrid Aromatic- Aliphatic Self-Assembled Monolayers of Fatty Acid

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Abstract ID #MTFC-0110

The control of surface properties on microscopic and macroscopic scales is an important scientific and technological issue which can be addressed by using ultra-thin functional films formed by the self-assembled monolayers (SAMs). It is well known that electron irradiation of SAMs provides an interesting alternative for high resolution surface patterning, and even more importantly, for formation of new 2D materials such as carbon-nanomembranes (CNMs), with potential application in different areas of nanotechnology such as ultrafiltration and nanobiosensing [1]. To understand the relation between the original SAM structure [2] and resulting CNMs formation [3], in the current study [4] we conduct systematic analysis of the electron irradiation process for a model SAMs deposited on Ag substrates and based on homologue series of biphenyl substituted carboxylic acids (C6H5-C6H4-(CH2)n-COO/Ag, n = 2-6) with different length of the aliphatic linker defined by the number n. Our results show that process of electron induced desorption, cross-linking as well as elimination of the SAM binding group depends on the parity of the parameter n (the odd-even effect). Our observations indicate a way for controlling thickness, porosity and purity of such nanomembranes, which are the key parameters determining the range of CNMs applications.

ACKNOWLEDGMENTS

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Development of Silver Chloride Based Antimicrobial and Antibiofilm Hard Coatings for Food Packaging Industries

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Biofilms-associated infections targeted by the persistence of food pathogenic bacteria possess a high health risk related to the treatment of antibiotic resistance [1]. In this regard, scientific communities come up with emerging strategies to slow down antimicrobial resistance and inhibit bacterial biofilms. Nanoparticle-based antimicrobials ((NAMs) provide a compelling alternative to antibiotic resistance of bacteria with great potential for bacterial growth prevention for foodborne contaminants in the food industry [2, 3]. Notably, silver halides (AgX) antimicrobial coatings provide a tailored concentration of biocidal Ag+ ions in an aqueous medium and thus inhibiting bacterial multiplication by denaturation of bacterial DNA, which affects the protein content and enzymes essential for bacterial cell growth [4].

In the present study, we explore the development of synergistic AgCl/ dimethyl-dodecyl-ammonium chloride (AgCl/DDAC) colloidal NAMs by a simple titration method that offers advantages for the safe, stable, green, and scalable production of a new generation of nanoantimicrobials. Herein, a silver- poly (vinyl methyl ketone (PVMK) water-insoluble nanocomposite coating was developed. Morphology and stability of the nanocolloids were investigated as a function of stability towards aging. Nanoparticle size distribution and hydrodynamic radius were measured by dynamic light scattering. NAMs were further characterized by transmission electron microscopy (TEM), X-ray photoelectron, and Uv-Vis spectroscopies. Antimicrobial ion release study of AgCl/DDAC/PVMK nanocoating done by the ETAAS study which supports a controlled release of silver ions. Real-time, in situ attenuated total reflection infrared spectroscopy (IR-ATR) was used to monitor microbial biofilm growth inhibition induced by the bioactive silver ions released from the nonantimicrobial coating. Our experimental evidence aids the morphological stability of the nanomaterial, along with their antimicrobial activity. The effect of the antibacterial and antibiofilm action of as-prepared synthesized materials was tested against Gram-positive bacteria Staphylococcus aureus (ATCC 29213), Listeria monocytogenes, and Gram-negative bacteria Escherichia coli (ATCC 25922), Pseudomonas aeruginosa (ATCC 27853). The results clearly indicate the AgCl/DDAC/PVMK based nanocoatings possess strong antibiofilm activity, aiming at bacteriostatic, long-term effects against tested foodborne pathogenic bacteria, being an optimal choice for active food packaging materials.

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Biological Properties of Silicate Based PEO Coatings on the Pure Mg

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Abstract ID #MTFC- 0129

Plasma electrolytic oxidation (PEO) technology could address the growing demand for Mg-based biomaterials with corrosion, erosion resistance, and biocompatibility. Fundamental properties of degradable materials are biocompatibility, controllable degradation rate, appropriate cell adhesion, and acceptable wear resistance [1]. The degradation behavior of PEO coatings in a biological environment depends on the oxide layer's microstructure and phase composition. Control of the initial degradation has paramount importance for the first days of the healing process after implantation. Protein absorption to the PEO coatings has particularly important for the adhesive and proliferative properties of cells. Appropriate adhesive properties relate to chemical stability and better corrosion performance [1].

The aim of our investigation was to apply PEO treatment for Mg-based material in a silicate bath with different voltage parameters to obtain bioactive surfaces with controlled degradation rate. The electrolytic bath (JP-1) consisted of 10 g/L NaSiO$_3$, 10 g/L NaOH, 5 g/L NH$_4$F. The use of different voltage values (150V, 200V, 225V) led to physicochemical characteristics of the coatings. The properties of the ceramic layers were evaluated with a scanning electron microscope (SEM), Energy-dispersive X-ray spectroscopy (EDX), roughness, and wettability measurements.

The cytocompatibility of the prepared coatings was determined using Human umbilical cord mesenchymal stem cells (UCMSC). UCMSC line was plated at a density of 40 000 cells/cm$^2$. Fluorescence microscopy was used for visualization and quantitative analysis of adherent cells to surfaces of Mg samples. The surface of each sample type was covered and performed with DAPI dye. DAPI acts through binding to DNA molecules and is used to detect and stain the nucleus [2]. Staining of cell nuclei with DAPI allowed for the display of UCMSC cells on coated and non-coated Mg surfaces.

Within a cultivation period of 24 h, the amount of adhesion UCMSC cells was higher on PEO surfaces compared with control. It has been clearly seen that the nucleus has a polygonal shape. In pure Mg samples, the nucleus has a round form that could indicate the apoptosis effect. A resazurin reduction assay evaluated cell viability on 1st day of cultivation. The resazurin reduction assay on day 1 exhibits the level of specimen cytotoxicity and cell attachment primarily, as proliferation is not yet intensive during this insufficient period time. Among the various test samples, JP-1-150V and JP-1-225V. Showed significant superiority over JP-1-200V in cell attachment at the end of one day of incubation.

We conclude the PEO coatings obtained at 150 and 225 V have potential properties for development of biocompatible Mg-based implants.

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The Concept of Miscellaneous DCSBD Plasma Technique Conditions to Accomplish Suitable Structural Properties of Tire Rubber

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Abstract ID #MTFC-0136

A model tire rubber blend was subjected to the diffuse coplanar surface barrier discharge DCSBD working in ambient air in order to investigate structural differenties. Additionally, a multiple plasma treatment conditions were performed. The first condition was the applied exposure time, when examined rubber was exposed to DCSBD plasma for 10 s, 30 s, 1 min and 1,5 min. Another factor was the location of the treated rubber on the plasma electrode and the chemical composition of model blend. The structural analysis was carried out by FT-IR spectroscopy using a diamond crystal by means of identification of novel functional bonded species. Furthermore, the elementary analysis was linked by EDX spectroscopy and morphology was studied by SEM microscope. Also the wetting properties were studied. Overall, the efficiency of DCSBD plasma source has been mostly proved to be suitable for blend surface modification in order to improve its surface structural characteristics mainly in lower exposure times. The authors would like to thank the Slovak Grant Agency KEGA for financial support (GRANT KEGA 001TnUAD-4/2022).
Plasma Electrolytic Oxidation in Amorphous Particle Suspensions as a Way to Improve Surface Texture and Bioactivity of the Oxide Coatings

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Abstract ID #MTFC-0139

Plasma electrolytic oxidation (PEO) is known as a novel and promising technique for preparation of chemically modified bioactive layers for implantology issues [1]. PEO process implies interactions between metallic anode and electrolyte at voltages 100 V or higher, leading to formation of porous oxide layer with high adhesive strength. Since the coatings formed do not exhibit appropriate biocompatibility, supplementary compounds (usually calcium phosphates) have to be introduced into electrolyte bath and subsequently incorporated. To date, two main groups of such compounds are known – soluble salts and solid particles, however, the latter are of greater interest nowadays due to those extended capabilities for imparting the desired phase composition of the coating [2]. Along with that, this technique remains poorly understood, as evidenced by the ambiguous relationships between the nature of particles, the evolution of the PEO process, and changes in the resulting oxide coatings.

Previous studies mainly focused on three different particle parameters – size, chemical stability and melting point. For example, it was proved that incorporation of micro- and nanosized particles occurs in a peculiar manner, leaving a significant mark on coating morphology, pore size and corrosion resistance [3]. In this study, we aimed at establishing the possibilities to modify various physicochemical properties and bioactivity of the PEO coatings, using particle crystallinity as a variable. PEO process was conducted in direct current mode at a voltage of 350 V in electrolytes containing stoichiometric crystalline hydroxyapatite or amorphous tricalcium phosphate particles with average size of ~0.5 µm. Analysis of coating surface included determination of wettability, roughness, chemical composition and topographic parameters of a wide range, while bioactivity was evaluated with simulated body fluid (SBF) tests. Additionally, repeatability of the results was estimated by fabrication of coatings on two different titanium-containing substrates.

Crystallinity of the calcium phosphate particles had an apparent specific effect on the hydroxyapatite layer growth dynamics during immersion in SBF solution and surface topography, which was reflected in the modification of the pore shape, average size, uniformity of pore size distribution, total surface porosity, average roughness, and the number of pores per unit area. Incorporation of amorphous particles turned out to have more positive effect on surface bioactivity, as well as allowed to create coatings with higher mass fraction of calcium phosphate phases. It was concluded that rough and developed surface of amorphous particles is responsible for a more positive outcome, also being the main factors that ease their entrapment into the porous structure of the oxide layer. Moreover, variation of particle crystallinity was proposed as a new instrument for modification oxide coating properties prepared with PEO in suspensions.

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Polypropylene Mesh Implants Modified By Nanostructured PVD Coatings

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Abstract ID #MTFC-0140

The use of various methods of anterior abdominal wall plastic surgery using mesh polymeric materials has been a revolution in hernia repair surgery and is the “gold standard” in the treatment of patients with ventral hernias [1]. The ideal synthetic mesh should be biocompatible, easy to handle and provide sufficient stability to prevent recurrence, degradation, or shrinkage. Despite the manufacturer’s claims, the differences between various types of meshes are unproven, and it is currently difficult to recommend any single mesh. Currently, intensive developments of new materials and substances that can improve the mechanical and biological properties of modern medical implants are being carried out [2].

In this sense, it is important to use the latest plasma technologies for the synthesis of a number of bioinert coatings based on niobium, tantalum, zirconium, titanium, and their oxides by ion-plasma vacuum-arc deposition using a high-frequency field at low temperature [3]. These coatings have the following characteristics: chemical and biological inertness, chemical resistance in acids and alkalis, no toxic reactions, no effect on the chemical composition and pH of tissue and cell fluid, and the ability to achieve continuity of the coating at a thickness of tens to hundreds of nm. The temperature of the coating does not exceed 50ºC, which does not lead to the loss of the polymer material of the prosthesis and its properties (in particular, the adhesion of the polymer base and the surface relief after coating.

In this research, thin nanostructured Zr and ZrO2 coatings were deposited onto polypropylene mesh implants for hernia repair surgery by using vacuum-arc evaporation with RF discharge in a Bulat-type facility. The structure, surface morphology, and phase composition of the obtained coatings have been investigated by means of optical and scanning electron microscopy, energy-dispersive spectroscopy (SEM + EDS), X-ray diffraction analysis (XRD), X-ray fluorescent analysis (XRF).

The experimental and clinical study on rats considering tissue response to the subcutaneous implantation of synthetic polymer endoprostheses with bioinert coatings has been carried out. The choice of a set of biochemical tests was due to the need to identify the intensity of the inflammatory process after implantation (glycorotene content) and assess the functional status of the liver (ALT, AST) and kidneys (urea, creatinine) and basic metabolites such as glucose total protein and cholesterol. In addition, the use of these indicators assessed the toxic effects of the implanted coated meshes.

REFERENCES


Optical and Electrical Properties of Prepared by Spray Pyrolysis CuMnO$_2$ Thin Films

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Abstract ID #MTFC-0145

Thin CuMnO$_2$ films have a p-type of electrical conductivity and a band gap $E_g \approx 1.55 - 1.7$ eV [1]. Compositional and structural changes of CuMnO$_2$ films make it possible to change the location of the Fermi level in the band gap, which leads to the modulation of all electrical properties of the films [2]. In photoelectrochemical reactions of hydrogen evolution with the participation of CuMnO$_2$, a high positive electrode potential with satisfactory stability is noted, which indicates the prospects of manufacturing high-quality solid-state heterojunctions with p-CuMnO$_2$.

Thin CuMnO$_2$ films of p-type electrical conductivity with a thickness of $\sim 0.3$ μm were made by spray pyrolysis of 0.1 M aqueous solutions of salts of copper dichloride CuCl$_2$∙2H$_2$O and manganese MnCl$_2$∙4H$_2$O. When dissolving metal salts, double-distilled water was used. Separately prepared solutions of copper and manganese salts before application were mixed in a ratio of 1:1 by volume using a magnetic stirrer for 30 min at room temperature. The pyrolysis temperature in obtaining samples of CuMnO$_2$ thin films on substrates of sodium-calcium glass and sital was $T_S = 350$ °C. Compressed air was used as the carrier gas. Before applying the CuMnO$_2$ films, the substrates were degreased in an ammonia-peroxide mixture H$_2$O$_2$:(NH$_2$)$_2$OH:H$_2$O, treated with a 5% solution of potassium dichromate K$_2$Cr$_2$O$_7$ in sulfuric acid. Samples of CuMnO$_2$ films made on 18×18 mm$^2$ glass were used to study the optical transmission spectrum. The spray pyrolysis process made it possible to simultaneously deposit films on different substrates. Specially made masks were used to obtain film steps, which were used to determine the thickness. The contact areas on the films were produced by depositing indium metal for a detailed study of the electrical properties. The resistivity of the formed indium contacts was less than 10 Ω·cm$^2$, which made it possible not to take into account the resistance of the contacts when analyzing the resistivity of the films.

CuMnO$_2$ films have a transmittance $T \approx 22 \div 24$% in the wavelength range $\lambda > 900$ nm. An analysis of the absorption spectra of the films indicates direct optical transitions. The optical band gap of the obtained CuMnO$_2$ films is $E_g = 1.65$ eV. The resistivity of the films at room temperature is $\rho = 1.8$ Ω cm. The activation energy of the conductivity of the CuMnO$_2$ films $E_a = 0.5$ eV in the temperature range 287 K < $T < 293$ K indicates the ionization of deep acceptor levels in the band gap. The increase in activation energy from $E_a = 0.21$ eV in the range of 292 K < $T < 359$ K to $E_a = 0.27$ eV at $T > 359$ K is associated with the activation of electrical conductivity through the grain boundaries. CuMnO$_2$ thin films (produced by an inexpensive spray pyrolysis method) can be used as a photoactive layer in photoconverters. As the frontal layer of heterostructures, it is necessary to reduce the resistance of the films by doping or shunting the frontal layer with transparent conductive oxides.

REFERENCES


Method of the AlN Films Planarity Estimating

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AlN films are often used as a seed layer in GaN/Al(Ga)N heterostructures grown on Si or Al2O3 substrates [1, 2]. Understanding their growth mechanism is therefore crucial for practical applications, including high-frequency devices. In this work, AlN films were synthesized by using RF-powered reactive magnetron sputtering of an aluminum target in a gas mixture of Ar and N2 (respectively 1:3.5). The substrate was n-Si (111) wafers with a resistivity (2-3)·10-3 Ohm·cm. Two groups of AlN films with thicknesses of 1 and 3 μm were grown. The samples were characterized using an optical microscope (Carl Zeiss NU-2E) and scanning probe microscope (NanoScope IIIa Dimension 3000TM). The surface micrographs of the AlN/Si samples are characterized by clear green rings alternating with black ones. They are visualized in specific places on the surface. The diameter of the observed rings varies from 5 to 10 μm. It was expected that in the places of occurrence of interference rings we have small pits of spherical curvature of the surface. The change in the depth of these pits provides the corresponding optical ways difference to form an interference pattern. But the AFM data showed different results. The places in which the "rings" visualized were not pits, but micro-hills and the viscosity-elastic properties of them do not differ from the rest of the surface. Thus, they are obviously chemically the same AlN film. The nature of their formation is most likely related to the peculiarities of thermodynamic processes at the chosen method of growing these samples. This statement is supported by the existence of the same islands only slightly lower in samples with the film thickness of 3 μm. The refractive index of the AlN film was obtained from ellipsometric measurements and correspond formulas for the radii of the light (dark) rings were obtained. Comparison of calculated and experimental data gives deviations for maxima (minima) of the second and third orders at the level of 0.6-3.6%. While for the lower and higher orders we have a noticeable increase in the mismatch ~ 4.5-5.9%. Most likely, this feature is due to the deviation of the surface of the micro-hill from the spherical curvature. This circumstance is, in principle, obvious, because the curvature of the contour of the formed "hill" changes unevenly and is subject to certain thermodynamic principles. But in the middle between the "top" of the hill and his "foot" we can assume that the decrease of the film thickness is linear. In our case, the number of observed rings on the micrographs is related to the height of the micro-hill – the increasing of the number of visualized "rings" is accompanied the increasing of the height. Control measurements by the atomic force microscopy showed that one visualized "ring" has ~ 100 nm of height. Thus, this method can be used to reject potentially unreliable AlN structures with a high degree of deviation from planarity.

REFERENCES

Nano-Heterostructured Materials – Based Sensors for Safety & Biomedical Applications

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Safety monitoring in Lithium-ion batteries (LIBs), as well as of volatile organic compounds (VOCs) in different environments, namely for safety applications, is a growing field due to the high reactivity of the used materials inside that requires specialized sensor structures [1, 2].

In this work, we summarize the detecting performances towards the battery solvents and VOCs of metal oxide heterolayer-based devices and propose a way to adjust the sensor selectivity by changing the nano-heterostructured materials. Oxides are grown by a chemical solution method and by thermal atomic layer deposition at various temperatures. Next, we study the morphology and structure, as well as electronic, chemical and sensor characteristics of the semiconducting oxide heterostructures. Gas sensing studies evidenced that coverage of oxide and forming of nano-heterostructured materials-based sensors is an efficient approach to improve the LIB electrolytes sensing. The present research shows that the combination of the ability to sense the electrolyte vapors used in LIBs and the size control provided by technological approaches makes these nano-heterostructures extremely attractive for battery safety control and biomedical applications.

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Application of Wear-Resistant Nanostructures Formed by Ion Nitridizing & Electrospark Alloying for Protection of Rolling Bearing Seat Surfaces

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The paper analyzes the works devoted to solving problems affecting the bearing life of rolling bearings (RB) and to revealing reserves for its increase [1]. Analyzed modern methods that affect the improvement of the surface quality of parts [2, 3]. There proposed a new technology for forming a protective coating on the shaft bearing journal neck or on the surface of a journal pressed thereon, which consists in the use of a combined technology comprising a process for stage-by-stage aluminizing by the method of electrospark alloying (AESA) [4] followed by a process of ion nitridizing (IN) [5]. Such a coating has a 100% continuity, the greatest thickness of the increased hardness zone of 300 μm, the surface microhardness of 7700 MPa, and the roughness (Ra) after non-abrasive ultrasonic finishing (NAUF) of 0.5 μm. The results of the X-ray microanalysis indicate that an increased content of aluminum is observed in the surface layer at the distance of up to 40 μm after the stage-by-stage AESA process. The research results have shown that in order to restore the shaft bearing journal neck surface layer hardness, which had been lost because of the repair work, the step-by-step AESA technology is more preferable. Thus, when removing the surface layer to a depth of 0.15 mm and subsequently carburizing by the method of electrosprak alloying (CESA), the maximum microhardness of the surface layer is 7250 MPa, and the thickness of the zone of increased hardness is 150 μm. At subsequently processing by the AESA method, these quality parameters of the surface layer are, respectively, 7350 MPa and 210 μm. The use of the NAUF method, both after CESA and AESA processes, makes it possible to reduce the surface roughness up to Ra = 0.5 μm. To decrease the surface roughness in the RB seating, it is advisable to practice burnishing with a diamond tool (DB) after the AESA process.

REFERENCES

Plasmonic Superhydrophobic Anti-Frosting Coating

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Abstract ID #MTFC-0166

Atmospheric frosting and icing pose significant performance and safety problems for critical and common-use infrastructure. Anti-frosting and anti-icing protection of exposed surfaces is a topic drawing continuous attention from researchers across many fields such as surface science, wettability, surface chemical and physical modification nanocomposites, and, more recently, plasmonics. Passive protection strategies, requiring no energy input, have been particularly sought. Even though several anti-frosting systems have been proposed, no viable and permanent strategy has been achieved.

Frosting in humid air is particularly problematic because most anti-icing strategies, of which many are based on superhydrophobic surfaces (SHS), fail due to frost formation. This happens because of the very nature of the micro–nanostructures involved. Condensing water on an SHS very likely leads to mechanical locking of ice instead of ice elimination. To counteract this, hybrid strategies involving some form of limited energy input are more and more considered, each with its challenges.

We propose a passive-active approach to bypass the intrinsic frost susceptibility of SHS coatings. The energy is remotely provided to a mesh of silver nanowires (AgNWs), protected against environmental degradation by a tin oxide (SnO\textsubscript{2}) shell [1]. The AgNW@SnO\textsubscript{2} core-shell structure is fine-tuned to enable a heat-intensive surface plasmon resonance of the nanostructure at a wavelength overlapping the emission maximum of blue laser light. By illuminating the protected surface with a low power blue laser, we can activate plasmonic heating of an underlying superhydrophobic epoxy-based nanocomposite [2]. The non-sticking behavior of submicrometric droplets of molten frost on the nanoporous AgNW@SnO\textsubscript{2} structure allows removing emerging frost droplets before they convert to a difficult to remove ice. We demonstrate the frost removal ability at –10 °C and 30% RH. In environmental stability tests, the coating exhibits high atmospheric, mechanical and thermal durability. The narrow wavelength absorption of the structure in the blue light range and reflective properties in the infrared range can prevent protected surfaces from overheating in direct sunlight.

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Nanoparticle Retention in Ambipolar Electric Field

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Abstract ID #MTFC-0171

Nanoparticle confinement conditions in capacitively coupled plasma with horizontal electrodes are quite well studied, but in the case of vertical arrangement of electrodes, a much weaker ambipolar radial field opposes gravity, and smaller particles can leave the plasma volume falling onto the dielectric wall of the discharge tube.

Nanoparticles present in plasma in large quantities and having acquired a negative charge can make a significant contribution to the ambipolar diffusion process. Ambipolar diffusion in a plasma consisting of electrons, positive ions, and charged nanoparticles has been the subject of a number of studies. However, analytical expressions for either the ambipolar field or the ambipolar diffusion coefficients are not given. We developed a model of ambipolar diffusion of a plasma containing electrons, positive ions, and charged nanoparticles. Analytical expressions are obtained for the ambipolar diffusion coefficients for all three charged plasma components, as well as for the strength of the ambipolar electric field.

We calculated the forces acting on a nanoparticle in radial direction for the plasma bulk region of RF capacitively coupled plasma with vertically arranged electrodes. Ion drag force $F_{id}$ does not have a significant effect on the nanoparticle movement in a wide range of their radius $a$. The gravity force and the Coulomb force are the growing functions of the particle size. However, the gravity force grows faster and for any value of $\delta$ there is the critical size, after which the particle cannot be confined by the ambipolar field. In a plasma consisting only of positive ions and electrons, the Coulomb force $F_{E,Amb}$ acting on a nanoparticle balances the gravity force $F_g$ at $a \approx 2.3 \, \mu m$. However, if there is even a little amount of negatively charged nanoparticles in the plasma, then the Coulomb force decreases and can hold much smaller nanoparticles only. Already at $\delta = 10^{-5}$ ($\delta = np/ne$ is the ratio of nanoparticle density to electron density) the critical size decreases more than twice. When $\delta = 0.002$ the equilibrium $F_{E,Amb} \approx F_g$ appears at $a \approx 210 \, \text{nm}$. Nanoparticles of approximately the same size were observed in our experiments. If the concentration of nanoparticles is significant then the Coulomb force further decreases and can even change its direction.
Electrical Properties of p-CuFeO$_2$/n-Si Heterojunction

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Delafossite (CuFeO$_2$) together with other minerals of its group is known for its wide range of electrical properties. Its conductivity can vary from insulating to metallic materials. CuFeO$_2$ is made up of comparatively abundant materials and could possibly be used as an absorber material in a solar cell or to reduce water in a solar water-splitting device [1]. This compound also belongs to the transparent conductive oxides (TCO). The development of p-type TCO will give us possibilities such as transparent p-n heterojunction, diodes, transistors [2]. Delafossite oxides have p-type semiconductor properties and rather low optical absorption for visible light [3].

Thin CuFeO$_2$ films (~100 nm thick) were obtained by high-frequency magnetron sputtering on glass substrates (for optical studies) and on plane-parallel n-Si plates (for obtaining heterostructures). A stoichiometric mixture of CuO and FeO$_2$ was used to make the target. This mixture was pressed into a special aluminum cup, the shape of the cup is chosen so that the plasma does not interact with the cup material. Spraying was carried out in a universal vacuum unit UVN-70, deposition process was in atmosphere of inert gas – argon. In order to obtain a film without impurities, a turbomolecular pump TMN-500 was used. Substrate temperature $t_S = 400$ °C, spraying was carried out in two stages $t_1 = 20$ min, $P_1 = 150$ W, $t_2 = 10$ min, $P_2 = 180$ W (t – spraying time, P – magnetron power). Studies of the optical transmission spectrum of thin CuFeO$_2$ films were carried out on an SF-2000 spectrophotometer in the wavelength range of incident radiation $\lambda = 0.2 \div 1.1$ μm. The surface resistance of CuFeO$_2$ films ($\rho_S = 30$ kΩ/□) was studied using the four-probe method. At a film thickness of 100 nm, its resistivity was $\rho = 0.3$ Ω·cm. The fabrication of ohmic contacts to CuFeO$_2$ films and n-Si substrates was performed using a silver-based conductive paste. Light I-V-characteristics were measured under integrated light under standard lighting conditions close to AM1.5, and with lighting power density of 80 mW/cm$^2$.

CuFeO$_2$ films have a transmittance $T \approx 31 \div 34\%$ in the wavelength range $\lambda = 0.5\div 1.1$ μm. Analysis of the absorption spectra of films indicates direct optical transitions. The optical band gap of the obtained CuFeO$_2$ films is $E_g = 3.22$ eV. An anisotopic p-CuFeO$_2$/n-Si heterostructure with a current rectification ratio of RR ~ 134 was fabricated. The diode characteristics of the heterostructure are due to the energy barrier $q\Phi_k \sim 0.5$ eV from the n-Si side. At forward biases of 0.05 V < $V$ < 0.2 V in the structure of p-CuFeO$_2$/n-Si the generation-recombination mechanism of current transfer prevails. At $V > 0.2$ V the tunnel mechanisms of current transfer with participation of surface states prevail. The reverse current at biases $-2$ V < $V$ < $-3kT/q$ V is determined by tunneling processes involving surface states. The p-CuFeO$_2$/n-Si heterostructure is photosensitive at reverse displacement under AM1.5 radiation conditions.

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Temperature Limits of the Existence of the Liquid Phase of Bismuth Particles in Contact with Nanocrystalline Vanadium Films

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Abstract ID #MTFC-0183

The existence of metastable supercooled melts is due to the necessity to overcome the energy barrier to form the new phase surface. Theoretical estimates of the value of maximum supercooling of free particles are 0.3–0.4 of the melting temperature.

For contact pairs, in which the melt is in contact with the solid phase, the crystallization temperature of the phase increases. This can be used to study the energetic characteristics of various interfaces. In applications, a melt below the equilibrium crystallization temperature is of interest for sensor technologies and should be taken into account when designing end devices.

During preliminary studies, it was shown that bismuth melts have unusual behavior. In contact pairs based on polycrystalline layers (Cu, Ag, and, probably, Al), the condensation mechanism determines its crystallization temperature. This effect was explained by the formation of a single system of inclusions in films deposited by the vapor-crystal mechanism. It is assumed that the grain boundaries of refractory layers play an important role in this. However, the similarity of crystallite sizes in Cu, Ag, and Al films complicates the study of this factor.

The work is devoted to the study of supercooling during crystallization in Bi/V films. Vanadium films are X-ray amorphous and consist of crystallites about 8 nm in size. It is several times lower than in previously studied samples. In doing so, the interfacial interaction in the selected contact pair turns out to be insignificant.

This makes it possible to estimate the influence of the microstructure of a refractory component on the particularities of crystallization of the supercooled melt. It is shown that the maximum supercooling does not depend on the method of bismuth condensation and reaches 0.3 of the melting temperature. Along with this, the mechanism changing of condensation from vapor-crystal to vapor-liquid changes the kinetics of crystallization. In the first case, crystallization begins at low supercooling and is observed in the temperature range of about 30 K. When being deposited into the liquid phase, the crystallization interval does not exceed 10 K. These differences are compared with the vanadium films morphology. The samples of the first series consist of particles about 500 nm in size. In the second series, the particle sizes are 50 nm. Meanwhile, in contrast to films in which refractory layers consist of crystallites of tens and hundreds of nanometers in size, avalanche-like crystallization was not observed even when bismuth was being deposited into the solid phase. In Bi/V films, no signs of the existence of a single system of low-melting inclusions, which causes the observed particularities of crystallization in the Bi/Cu, Bi/Ag, and Bi/Al systems, were found. This indicates the decisive role of grain boundaries and grain-boundary segregation in the formation and further behavior of bismuth-based condensates.
Magnetic Field-Assisted Molecular Beam Epitaxy of Fe(001) Films on MgO(001)

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Abstract ID #MTFC-0213

Molecular beam epitaxy (MBE) is a powerful tool in modern thin film technologies, including electronic, optoelectronic, spintronic or sensoric application. The structural properties of functional layers depend on the elementary steps of the MBE process that include adsorption/desorption, surface diffusion, nucleation/coalescence and, finally, the way of film growth. In the traditional MBE technology these elementary steps are controlled by substrate temperature, deposition rate and partial pressure of reactive gases. Applying the magnetic fields (MF), although uncommon for ultra-high vacuum (UHV) MBE growth, should not be ignored in the synthesis, processing of thin films, especially in ferroic systems [1]. Whereas post-deposition annealing under MF at high temperatures is known as a method of shaping desired magnetic anisotropy, engineering of magnetic properties using MF-assisted MBE remains unexplored. In the present contribution we report on the first attempts of growing magnetic films under external MF.

Fe(001) films were grown on MgO(001) substrates in a multi-chamber UHV system (base pressure $5 \times 10^{-10}$ mbar), including MBE facility and standard surface characterization techniques. Combination of “flag-style” (FS) and PREVAC[2]-style sample holders (the latter including permanent magnets for generation of MF) and a sophisticated two-station 4-axis manipulator allowed us an easy transfer of the substrate between the station proper of a given preparation step (cleaning, deposition, annealing). After each preparation step the sample could be in situ controlled using Low Energy Electron Diffraction (LEED), whereas magnetic properties were measured using magneto-optic Kerr effect (MOKE) and Conversion Electron Mössbauer Spectroscopy (CEMS).

The role of the external magnetic field for the magnetic anisotropy was revealed by measuring the full in-plane angular dependence of the hysteresis loops for MF applied during deposition along the Fe easy [100] and hard [110] in plane axes, using a sample deposited without MF as a reference.

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Oxidation Resistance of Fe on Ru(0001) – the Role of the Substrate and Preparation Conditions

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Epitaxial iron oxide films, with the stoichiometry from FeO (wustite), through Fe₃O₄ (magnetite), to α-Fe₂O₃ (hematite) are our current interests [1, 2] due to their unique electronic and magnetic properties, phase transitions and wealth of surface structures, which makes them materials with high application potential in spintronics and catalysis. Epitaxial films, when grown as the ultrathin ones, gain additional degrees of freedom, which allow to modulate their properties thanks to the high contribution of the surface low coordinated atoms, finite size effects (dependence of the structural, electronic and magnetic properties on the thickness) and last but not least interaction with the substrate (interfacial strains and reactions). Iron oxides films on Pt(111) and Ru(0001) substrates are of particular interest [1, 3], and comparison of these two systems was recently done in our group. In the present contribution we focus on the iron oxide films in the ultrathin limit, with special attention to the FeO stoichiometry, for which we have previously shown a metastable ferromagnetic phase under normal conditions [1]. The iron oxide layers with the intended FeO stoichiometry were grown in a multi-chamber ultra high vacuum system on the Ru(0001) single-crystal substrate either by the oxidation of a few monolayer metallic Fe deposit or by reactive deposition of Fe under a background pressure of molecular oxygen. The films structure and morphology were characterized in situ by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). The main tool of phase identification was in situ conversion electron Mössbauer spectroscopy (CEMS), which could be implemented with sub-monolayer sensitivity and resolution for films deposited using the ⁵⁷Fe isotope.

Regardless of the preparation recipes, films with a nominal thickness of 2 FeO monolayers (ML) grew as continuous layers with a characteristic moiré structure due to the film-substrate misfit, seen in LEED patterns and STM images. Room temperature CEMS measurements documented an oxide film in the paramagnetic state and the electronic structure markedly different from bulk FeO.

Beyond the 2 ML thickness we observed considerable resistance of iron against oxidation. For reactive deposition under an O2 partial pressure from (5x10⁻⁸ to 1x10⁻⁶) mbar – the highest being enough to obtain magnetite films on Pt(111), the films showed morphology of nanowires (up to 1 μm long and few tens of nm wide), whose dimensions, including height and density, depended on the iron dose and the deposition conditions. Similar structures were previously observed by Monti [3]. CEMS spectra unambiguously identified the nanowires as composed of metallic Fe. Post-deposition oxidation of metallic Fe films led to similar results. We explain the observed striking differences for the Pt and Ru substrates in terms of the structural and chemical properties of the double-layer FeO films.

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REFERENCES

Defect Nanostructure and Its Impact on Magnetism of α-Cr₂O₃ Thin Films

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Abstract ID #MIFC- 0219

Thin films of the magnetoelectric insulator α-Cr₂O₃ are technologically relevant for energy-efficient magnetic memory devices controlled by electric fields [1-3]. In contrast to single crystals, the quality of thin Cr₂O₃ films is usually compromised by the presence of point defects and their agglomerations at grain boundaries, putting into question their application potential. Here, we experimentally investigated the defect nanostructure of magneton-sputtered 250-nm-thick Cr₂O₃ thin films prepared under different conditions on single crystals of Al₂O₃ (0001) and correlate it with the integral and local magnetic properties of the samples [4]. We evaluated the type and relative concentration of defects. For this purpose, positron annihilation spectroscopy (PAS) was used as a unique probe for open-volume defects in thin films. The results obtained for the thin-film samples are compared to single crystal data. Our analysis reveals that the Cr₂O₃ thin films are characterized by the presence of complex defects at grain boundaries, formed by groups of monovacancies, coexisting with monovacancies and dislocations. The concentration of complex defects can be controlled by the sample fabrication conditions including the deposition temperature as well as the post-annealing in vacuum or in air. The defect nanostructure strongly affects the magnitude of the electrical readout, which is measured of the Cr₂O₃ samples capped with a thin layer of Pt relying on spin Hall effect [5]. Furthermore, the presence of larger defects like grain boundaries has a strong influence on the pinning of magnetic domain walls in thin films. Independent of these findings, we showed that the Néel temperature, which is one of the important technological metrics, is hardly affected by the formed defects in a broad range of deposition parameters. Namely, our data suggests that the manipulation of the antiferromagnetic domain pattern in thin films of Cr₂O₃ can be done by adjusting the grain structure of the fully relaxed Cr₂O₃ thin film without any detrimental effect on its operation temperature. Our results pave the way towards the realization of spin-orbitronic devices where magnetic domain patterns can be tailored based on defect nanostructures without affecting their operation temperature.

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REFERENCES

Gradient (Si,N):DLC Layers for Improved Performance of Hip Joint Replacement Implants

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Abstract ID #MTFC- 0223

Biomaterials that replace diseased bones have particularly strict requirements for both biological response and mechanical properties. The latter is especially emphasized for surfaces that mimic lost joints, as combination of friction and biological fluids constantly degrade the material. The resulting wear and corrosion, including fretting corrosion, disturb surrounding tissue by release of wear particles and toxic ions that may trigger inflammatory response. Chronic inflammation promotes formation of fibrous tissue and osteoclast differentiation, which can threaten the stability of implanted device.

To counteract that processes, several surface treatments of medical grade titanium alloys have been proposed in recent years. These include carbon layers, titanium oxide layers, carbide and nitride based layers that are characterized by increased hardness and wear resistance, while not causing adverse tissue reactions. Among carbon layers, the family of amorphous DLC layers hold distinct advantages over the other options, as their properties can be tuned by changing sp2/sp3 carbon atom ratio or alloying with other elements.

Our work explores this flexibility to deposit gradient (Si,N):DLC layers on Ti6Al7Nb medical alloy, utilizing Radio Frequency Chemical Vapor Deposition (RF CVD). The research aims to enhance and prolong the performance of bone implants, subjected to tribological action in biological environments. Obtained structures underwent chemical analysis by EDS, XPS and Raman spectroscopy, as well as microstructure and topography imaging by SEM, optical profilometry and AFM. Corrosion resistance (impedance spectroscopy), mechanical (nanoindentation) and tribological parameters were compared to unaltered Ti6Al7Nb alloy to assure improved functional properties. Lastly, the DLC layers were tested in terms of biocompatibility, followed by analysis of type and concentration of ions leeched to the media via ICP-MS.

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Dying Method for Oxide Coatings Produced by Plasma Electrolytic Oxidation of Magnesium and Aluminium Alloys

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Abstract ID #MTFC-0225

There are many methods to protect metal alloys against corrosion, e.g. plasma spraying, thermal spraying, organic coatings or electrochemical treatments. In the modern world, the emphasis on the quality of the surface finish from the clients is stronger than ever. The requirements of the market are increasing while the use of sustainable technologies is becoming a necessary pre-requisite to deliver the new product to the customers. It is why this research is focused on the use of plasma electrolytic oxidation (PEO), a plasma-assisted electrochemical surface treatment, to give rise to colourful oxide coatings on two metallic substrates: AZ91 magnesium alloy and AW-6061 aluminium alloy.

PEO provides a means to produce protective, relatively thick and hard oxide coatings on these substrates, however, it lacks the ability to produce a wide array of colours. Typical PEO oxide coatings are white or grey. If there are additional ‘colouring’ salts in the electrolytic bath (e.g. vanadates, manganates, copper or nickel compounds), there is a possibility to bring about a different hue. Nevertheless, the addition of these salts always impact other properties of the coatings as well, like their microstructure or thickness, so the modifications to the original processing parameters need to take place. Therefore, in the work the authors present an easy-to-conduct method for producing colourful coatings in an environmentally friendly process of PEO with the use of solvent dyes. The colouring step here is not happening in the process bath so the dispersion of the dyes to the waste-water is minimal. The whole processing procedure takes place as follows. First, the coatings are produced in the alkaline solution of silicate, phosphate or borate salts (or a mixture of these). Next, the produced coatings (white or light grey) are carefully dried and then subjected to the dye solution for 2-5 minutes. Then, the samples are allowed to drip and dry. The final step is the immersion of the coatings back to the PEO bath and the process is continued for the next 15-30 seconds. Such a procedure allows for the uniform colouring of the specimens because the excess of the dye is incinerated in the plasma sparks during the PEO processing. If the colour is too dim, the procedure can be repeated a few times.

In the research, the authors studied a variety of different concentrations of the dye as well as different processing routes. The coatings were then subjected to thorough investigation using microstructural methods (SEM, Ra), chemical composition analyses (SEM/EDS, XRD, Raman) as well as corrosion testing (EIS). The process was also investigated with the use of in situ optical emission spectroscopy, to analyse the plasma emissions during the sealing of the colorants inside the oxide pores.

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Chemical Conversion Coatings Pre-Treatment as a Viable Method for Influencing The Properties of Oxide Films Produced by Plasma Electrolytic Oxidation of Light Metal Alloys

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Light metal alloys (e.g. Al and Mg) are important materials for the transport applications because of their favourably high strength-to-weight ratio that can be directly translated to lower power consumption and emissions of CO2 to the atmosphere. It is crucial to provide proper surface treatments to the structures based on these materials due to their propensity to undergo corrosion. There is a wide array of methods that provide a way to limit the corrosion rate of the substrate and the most effective ones are those relying on hexavalent chromium. Of course, there is an ongoing need to eliminate this carcinogenic/mutagenic chemical from the industrial use, so the demand on the alternative solutions to the problems is getting more pressing over time.

Plasma electrolytic oxidation (PEO) is one of the niche methods for protecting light metal alloys since it resides on the bridge between electrochemical and plasma-based treatments. It allows for the formation of relatively thick, hard and porous oxide coatings by anodic oxidation of metal workpieces in passivating electrolytes to the voltages so high, that the dielectric breakdown of the grown oxide is possible. In the wake of the breakdown, the so-called ‘micro-discharges’ are supporting the non-faradaic oxide growth and make it possible to incorporate the electrolyte species into the oxide coatings. Although the method has some advantages it is not perfect. First of all, the method is highly energy-consuming, which impedes its widespread commercialization. Moreover, the complexity of the concurrent processes taking place during the surface treatment are very sensitive to the experimental conditions.

In this research we focused on the possibility to lower the power consumption of the process by a pre-treatment which was the formation of a thin chemical conversion coating (CC) on AW-6061 aluminium alloy and AZ91 magnesium alloy. The CCs were formed in the conventional processes that are used for the anticorrosion purposes. They were based on the submersion of the samples in the alkaline solutions of K2Cr2O7 (a reference) and other alternatives compositions: K2ZrF6, K2TiF6, Na2MoO4·2H2O, K2MnO4, (NH4)2Ce(NO3)6, CeCl3·H2O, Ce(NO3)3·6H2O and NaVO3. The presence of the CC before PEO allowed for the instantaneous ignition of ‘micro-discharges’ without the need for the inefficient electrochemical formation of the oxide in the first dozens of seconds of the process. Then it was observed that the application of the CC significantly lowered the time needed for the initiation of the so-called ‘soft-sparking’ which is a special type of regime in the PEO processing occurring at lower voltages (reduced energy consumption) making a more promising alternative for commercial implementation. In the research, the authors utilized techniques like SEM, EDS, XRD, Raman, OES and EIS corrosion investigations to determine the effect of the PEO processing with the CC pre-treatment on the properties of the oxide coatings.

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Conference Track: “Multifunctional Thin Films & Coatings”
Superior Corrosion Resistance of the Oxide Coatings Produced by Plasma Electrolytic Oxidation of Aluminium and Magnesium Alloys Modified by Selected Corrosion Inhibitors

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Abstract ID #MTFC-0227

Corrosion is one of the biggest challenges of the post-industrial evolution world since it touches upon almost every aspect of modern civilizations development. Aluminium and magnesium alloys are important materials in the modern world because of their low weight. Appropriate alloying makes the alloys significantly stronger than their counterparts, however the presence of chemically dissimilar phases emerges the problem of corrosion. Therefore, the need of active corrosion protection is one of the biggest issues with metal alloys. It means that they should remain protected even when the coating loses its mechanical integrity, so called ‘smart coatings’.

In this research the authors attempted to prepare porous oxide coatings on AW-6061 aluminium alloy and AZ91 magnesium alloy which were then treated with selected corrosion inhibitors (CIs in short; e.g. acrylic acid, vinyl acetate) to provide a way to serve as ‘smart coatings’ to the underlying substrate. The coatings were prepared in the process of plasma electrolytic oxidation (PEO) which is an electrochemical/plasma surface treatment that utilizes voltages breaching the dielectric breakdown potential of the electrochemically grown oxide in a passivating electrolyte solution. In this study the authors investigated the coatings prepared in the silicate, phosphate and borate solutions (including their mixtures) to see which gave rise to the porous oxide coatings serving as the best reservoirs for the CIs. The coatings were formed under the asymmetric AC regime (AC PEO). After the ‘unloaded’ coatings were prepared, they followed one of the possible processing routes. The first one encompassed the use of the DC sealing treatment which was dipping of the PEO-coated specimens in the solutions of CIs in an alcohol for 2 min, followed by drying in air and then putting the samples in the PEO setup once again. After the connections to the setup have been established they were polarized linearly to 400V for 1 min and then they were held at that voltage for the next 4 min to finish the process. The other method was the AC PEO route. The first segment of the sealing was the same (dipping in the CI solution followed by drying and putting back to the PEO setup). Next, the samples were subjected to continued AC PEO for the next 15 or 30 s to quickly close the pores loaded with the CI and not to allow for the high temperature to destroy the organic compounds.

The resulting coatings were characterized from the point of view of the change caused by the additional treatment in the case of their microstructure (surface and cross-section porosity, thickness, roughness), chemical composition (SEM/EDS, XRD, Raman spectroscopy) and corrosion resistance (tests in a 0.1M Na₂SO₄+500 ppm NaCl). In addition, in situ optical emission spectroscopy was carried out to see if there were specific plasma emissions owed to the presence of CIs in the coatings during the electrochemical sealing procedure.
Effect of CaP-particles on Ceramic-Like Coatings Formed on Magnesium via Anodisation

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Successful bone regeneration is a complex physiological process that leads to the formation of new functional bone tissue. Bone formation around the orthopedic implants is the special focus due to numerous complications in the postoperative period. Biodegradable implants (particularly Mg-based prosthesis) open new perspectives in regenerative medicine but suffer from fast uncontrolled degradation [1]. Plasma Electrolytic Oxidation (PEO) technology could be ideal for degradable implant modification with enhanced wear and corrosion resistance, improved biocompatibility, and biodegradability [2].

Recent designs of the PEO procedure are focused on using CaP-particles suspensions, aiming at in-situ incorporation or sealing the porous coatings and endowing the layers with new functionalities [3]. In our investigation, we used the strategy of particle incorporation into the coating with no formation of a new phase. Preservation of the particle's primary chemical composition, shape, and size allows producing a high biocompatible surface with enhanced wear resistance.

The magnesium samples were treated in a silicate-based solution with the addition of the crystalline commercial spray-dried stoichiometric hydroxyapatite (Ca10(PO4)6(OH)2, HAP) powder and amorphous tricalcium phosphate ((Ca3(PO4)2, TCP) powder. Obtained coatings were analyzed by scanning electron microscope (SEM) technique, contact angle, and roughness measurements.

SEM images revealed particles' incorporation into the coating with location on the surface and inside the pores of the ceramic layer. The HAP addition to the solution resulted in the increasing roughness and wettability parameters. A preliminary investigation demonstrated the potential of a new HAP ceramic coating for medical application.

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REFERENCES

Diffusion-induced Phase Formation in Ni/Ti Layered Stacks

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NiTi nanostructured thin films are one of the most well-acknowledged representatives of the functional materials with shape memory effect (SME) [1]. A unique set of properties such as biocompatibility, superelasticity, high damping capacity, and chemical resistance determine the high potential of NiTi for microelectromechanical systems (MEMS/NEMS) applications [2]. NiTi thin film exhibits small thermal heat/cool mass as compared to NiTi bulk which results in a reduced response time and an increased operation speed that are especially attractive for applications in SME-based small-scale microactuators, microvalves, micropumps, etc.

However, the widespread use of thin-film NiTi is limited by the elevated temperatures (> 500 °C) needed to form a crystalline austenitic B$_2$-NiTi structure and achieve the SME, while immediately after deposition, the material usually has an amorphous structure [3]. The application of high temperatures is undesirable due to its probable negative effect on the morphology and long-term functionality of thin-film structures.

The motivation of the present study is to achieve the formation of the NiTi crystalline phase at low temperatures through the grain boundary mediated atomic diffusion. For that reason, the deposition of layered Ni/Ti stacks with post-deposition low-temperature annealing in a vacuum is proposed to form an equiatomic crystalline NiTi phase. Furthermore, the following two pathways are proposed for the realization of the scenario of lowering the onset temperature of B$_2$-NiTi phase formation: (i) to create an increased number of interfaces between Ni and Ti while keeping the same total thickness of the multilayer, when the generated mechanical stresses could be an additional driving force for the grain boundary diffusion, and (ii) to introduce an additional layer of noble metal (e.g., Ag, Cu) in-between the Ni and Ti layers to intensify the grain boundary diffusion by the additional stresses arising due to the difference in the crystal lattices and thermal expansion coefficients of layers.

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Improvement on the Microstructural and Nanomechanical Properties of (TiAlZrNbY)N-based Multiphase Coatings by Compositional and Structural Design

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Abstract ID #MTFC-0262

New multifunctional coatings can be developed based on a multiphase approach. Multiphase nanocomposite films tend to be dense and fine-grained because columnar grain growth is interrupted by the nucleation of another phase. The presence of a large amount of interfacial area in multilayer structures can increase hardness and wear resistance. Multicomponent coatings with different metallic and nonmetallic alloying elements combine the benefit of individual components leading to further development of coating characteristics. The potential for the advancement of new multifunctional coatings is very large, using materials with good tribological properties as individual layers of the multilayers, as well as making use of multicomponent coatings. Titanium aluminium nitrides based on γ-TiAl phase are considered for high-temperature applications, especially as thermal barrier protections for titanium alloys [1]. The properties of the TiAlN that make them attractive as a coating include outstanding oxidation resistance, low density and microstructural stability at elevated temperatures derived from their crystal structure nature. The performance of conventional TiAlN coating can be further improved by adding to its composition some transition metals, in particular, zirconium (Zr) [2], niobium (Nb) [3] and yttrium (Y) [3]. The addition of Zr to TiAlN-matrix causes further structure stabilization. The three metallic components possess different atomic radii and different electronic configurations and lead to the behaviour observed in solid solution hardened materials. The introduction of Nb in TiAlN significantly improves the wear resistance and changes the predominant wear mechanism of the material from adhesive wear with fatigue wear (active cracking) to abrasive wear with fatigue wear as a result of the formation of fcc lattice solid planes (111) in the crystal structure. The incorporation of Y to TiAlN-matrix leads to extensive grain refinement and a more equiaxed structure due to the continuous nucleation process.

The purpose of this investigation is two-fold. First, to study the structure of (TiAlZrNbY)N coating, including an examination of its multiphase composition, distribution of elements in the coating nanolayers and functional properties. Second, to consider the changing in structure and properties when multilayer multiphase (TiAlZrNβY)N/TiAlZrNbY and (TiAlZrNbY)N/CrN coatings are formed.

Results of the experimental data show the following advantages of multilayer multiphase coatings: (1) the greater resistance to microchipping and material pullout during adhesion strength testing; (2) the reduction of adhesive wear because of nanoscale crystalline structure as opposed to the columnar grained structure of a single thick multiphase coating; (3) the minor delamination of fine-scales on the surface of a multilayer coating with no evidence of plastic deformation and perpendicular crack propagation during wear testing.

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Formation of Oligoperoxide Coatings on the Amorphous Alloys

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The development of modern technologies is associated with the modification of metallic surfaces in order to give them specific physical and chemical properties [1]. One of the modification methods is the formation of thin film from a solution of heterofunctional oligoperoxide (HFO). Modifying amorphous metallic alloys (AMA) with oligoperoxides can be used to form protective coatings and immobilize various monomers and drugs. However, the efficiency of such modification depends on the surface properties of oligoperoxides and amorphous metallic alloys [2].

For the chemical modification of the surface of Fe\textsubscript{78.5}Ni\textsubscript{1.0}Mo\textsubscript{0.5}Si\textsubscript{6.0}B\textsubscript{14.0} and Fe\textsubscript{73.1}Cu\textsubscript{1.0}Nb\textsubscript{3.0}Si\textsubscript{15.5}B\textsubscript{7.4}, we used \((0.5...5.0)\times10^{-3}\) M aqueous-ammonia solutions of a heterofunctional oligoperoxides based on vinyl acetate (VA), 2-tert-butylperoxy-2-methyl-5-hexen-3-yne (VEP) and maleic anhydride (MA) taken in the following ratio: VA:VEP:MA = 1:1:1. The quality of applied oligoperoxide coatings on metallic surfaces was investigated by electrochemical impedance spectroscopy in 0.5 M aqueous NaCl solution. The electrochemical impedance spectroscopy (EIS) was realized with the help of an Gamry Potentiostat Reference 600. It is established that the surface layers of modified amorphous alloys have higher resistance values. This indicates the formation of dense surface coatings. It was found that denser coatings are formed on the external surfaces of Fe-based amorphous alloys. Higher affinity of oligoperoxide layers to Fe\textsubscript{73.1}Cu\textsubscript{1.0}Nb\textsubscript{3.0}Si\textsubscript{15.5}B\textsubscript{7.4} alloy was confirmed [3] and the quality of the coating was dependent on the duration of its formation.

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Structure, Optical Properties and Photocatalytic Activity of Undoped, Nd-Doped ZnO Films

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Zinc oxide is an important material due to optical, photocatalytic and magnetic properties that have been used in a variety of applications such as UV absorption, sunscreen lotions, antibacterial treatments, catalysts, photocatalyst etc. [1]. But these properties of ZnO strongly depend on the impurities and defects. It is well known that the existence of defects in a semiconductor would lead to corresponding defects energy levels in the band gap. Doping methods have been extensively utilized for modifying the ZnO electronic structure to achieve new or improved catalytic, electro-optical, magnetic, and other chemical and physical properties. Dopants can segregate on the ZnO surfaces or they can be incorporated into the lattice, where the dopants can be substitutional or interstitial or both. Doping in ZnO with a suitable dopant can make it more or less efficient in photodegradation of organic and toxic pollutants. Among the rare earth metals, Nd is one of the most widely used elements. Nd3+ doping reduces the band gap energy and enhances the possibility of the photodegradation of dyes under visible [2] and UV light.

Undoped and Nd-doped ZnO films were sputtered on silicon and glass substrates using the universal vacuum unit UVN-70. Before the sputtering, the vacuum chamber was pumped to a residual pressure of 5·10⁻⁵ mm Hg. Compressed ceramic tablets of pure ZnO and ZnO:Nd2O3 5 and 10 % wt. were used as targets and were deposited in an Ar atmosphere by radio frequency magnetron sputtering at a power of 200 W. To deposit the films, substrates were heated to 350 °C.

We investigate the X-ray diffraction patterns of undoped and Nd doped ZnO films on a “Dron-3M” X-ray diffractometer. At all samples reveals only peak around 2θ = 34.4° that correspond to reflection from (002) plane, i.e., the crystallographic c axis of the ZnO lattice is perpendicular to the substrate plane, and that means of high degree of texturing of the films. The XRD patterns do not show any other peaks corresponding to Nd, Nd2O3, NdO or any other additional phases associated with impurities. A detailed analysis of the position of the reflection maximum (002) revealed that Nd doping showed a decrease in the diffraction angle (002), which corresponds to the inclusion of Nd in the ZnO cationic sublattice, and rise of the interplanar interval and an increase in the lattice period. Also it worth to note that the increase of Nd concentration results the decrease of crystallite size and increase in disorder effect which resulted in the broadening and decrease of intensity of the XRD peaks.

The effect of doping was studied by UV-vis spectroscopy in the range of 200–1100 nm using a SF-2000 spectrophotometer. The Nd-doped ZnO films showed a shift toward the longer wavelength region, which indicates a decrease of the band gap energy contrary to the undoped ZnO film.

The influence of Nd on photocatalytic activity of ZnO films will be presented and discusses in our report in detail.

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The Process of Poly (4-vinylpyridine)-CoBr$_2$ Complex Formation in Both Static and Dynamic Conditions

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Abstract ID #MTFC-0299

Both static and dynamic formation of thin functional magnetic films of polymers crosslinked with single ion magnet complexes was thoroughly investigated. This approach is novel compared to the usual deposition of Single Ion Magnets from crystalline form. The investigated material has promising potential applications and is easy to process since it is formed on the surface of thin spin coated polymer (Poly(4-vinylpyridine)) film after dipping it into CoBr$_2$ solution [1]. What is more, the studied material showed astonishing qualities in organic field-effect transistor-like geometries with proven conduction increase by four orders of magnitude [2].

In order to think about applications, it was necessary to characterize fully the process of the complex formation and its dependence both on the concentration of the cobalt salt solution and on the time of immersion.

We proved that the geometry of the wrinkled topology [3] formed by the layer is directly related to the cobalt concentration on the surface measured by Secondary Ion Mass Spectrometry (SIMS). Both in the static and kinetic experiment a double process was observed, only the second of which coincides with the appearance of the wrinkles. It is described by two breakthrough mechanism [4] according to which wrinkled topography is formed in dynamic process. Presented data are supplemented by Atomic Force Microscopy (AFM) images.

REFERENCES

Synthesis & Characterization of WN/TiSiN Nanocomposite Multilayer Coatings

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Abstract ID #MTFC-0308

Based on the analysis of the scientific literature, one can conclude that single-layer coatings of tungsten nitride (WNx) show high hardness, melting point, electrical conductivity, and chemical stability. Despite the attractive characteristics of WNx for use as wear-resistant coatings and all the advantages of a multilayer architecture, only a few PVD multilayer systems based on tungsten nitride in combination with various transition metal nitrides have been investigated so far, i.e. WN/TiAIN [1], WN/CrAlSiN [2], WN/NbN [3], etc. Depending on the second layer's material, such coatings demonstrated higher hardness, oxidation resistance, or wear resistance. Thus, although WNx plays a crucial role in the high performance of multilayer nitride coatings, the second layer is also undoubtedly significant [4]. Nanocomposite nitride coatings with nanocrystalline grains (< 100 nm) embedded in the amorphous matrix are successfully utilized for cutting difficult-to-machine materials. Among them, the Ti-Si-N is one of the most well-known industrially used coatings with a low friction coefficient, high thermal stability, and oxidation resistance [5]. Therefore, new multilayer coatings based on Ti-Si-N and WN are expected to have increased mechanical strength and enhanced tribological characteristics.

The present work deals with the effect of the bilayer period of individual WN and Ti-Si-N layers on the microstructure, phase composition, and mechanical and tribological properties of WN/Ti-Si-N multilayers. The multilayers were deposited on tungsten carbide (WC/Co) substrates by magnetron sputtering from W (purity 99.95 %) and Ti50Si50 (purity 99.5 %) targets. The cross-sectional morphology of nanocomposite multilayer coatings was characterized by scanning electron microscopy and transmission electron microscopy. The hardness and wear resistance of multilayers were investigated using the nanoindentation and ball-on-disc method. We would like to emphasize that, such WN/Ti-Si-N multilayers have not been studied yet.

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Nanostructures Formed on a Gold Nanolayer Surface as a Result of the Impact of Highly Charged Xe Ions

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Abstract ID #MTFC-0311

Swift heavy ions (SHI) have been used since the 1970s for bulk and surface modification of materials for industrial use [1]. On the surface, with which these ions collide, nanostructures in the shape of a hillock or crater can be formed. Unfortunately, these ions often also damage the substrate of materials, which is related to kinetic energy transferred to the materials electronic subsystem. In collisions of slow highly charged ions (HCI) with a surface material only a small surface volume is excited within a few nm\textsuperscript{2}, because the kinetic energy of the ions limits the depth of neutralization of the potential energy of the ions to a few nm and causes that a very large amount of energy (10÷100 eV / atom) is deposited in a very short time. Despite the large difference in energy between SHI (kinetic energy in the range of MeV–GeV) and HCI (potential energy in the range of eV–keV), the coupling of the ion-induced electronic excitations to the lattice atoms is based on a similar mechanism. In the case of interaction of slow HCI this leads to atomic motion and nanostructure formation only on the surface without creating additional ionization and electronic excitation in the substrate along the ion’s path [2].

Gold nanolayers with a thickness of 50 nm and 100 nm deposited on a silicon or quartz substrate were irradiated by slow (in the range of 10÷100 eV) highly charged Xeq\textsuperscript{+} (q = 25, 30, 35, 36, 40) ions at the Kielce EBIS facility of the Jan Kochanowski University (Kielce, Poland), under high vacuum (10⁻⁸ mbar) conditions. The AFM images of irradiated surfaces allowed for the first time to unambiguously identify nanostructures in the form of craters and hillocks on the gold surfaces [3, 4]. The experimental results were compared with the theoretical calculations using: the inelastic thermal spike (iT-S) model and molecular dynamics (MD) simulations [5], and compared with the experimental data obtained for slow single ionized Xeq\textsuperscript{+} hitting Au surface [6]. Also using the micro-staircase model, theoretical predictions clearly showed that both the kinetic energy of highly charged ions and the potential energy have an influence on the type and size of nanostructures obtained on metallic surfaces. The interplay of these two energies is described by the critical ionic velocity. For the ionic velocities lower than the critical one the model assumes an appearance of the hillocks, while for the larger velocities a dominant surface structures are craters [7].

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Conference Track: “Multifunctional Thin Films & Coatings”


Characterization of Ti-Zr-Mo-C Films by Magnetron Sputtering: Microstructure, Chemical Bonding and Tribo-mechanical Properties

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Surface thin films have been used as protective and functional layers in various engineering fields for many years. The current trend for PVD technology is to develop transition metal carbides (TMC) films. It has been learned that TMC films show improved strength, toughness, wear-resistance, chemical inertness and conductivity [1]. Niobium is a corrosion-resistant material which is expected to be biocompatible in the living body. Niobium, when alloyed with titanium or zirconium can produce, in the proper concentration, a superconducting metal, and is thus used primarily in non-medical applications. The presence of zirconium in niobium results in higher mechanical properties. The addition of titanium to niobium reduces the melting temperature making it easier to process. The presence of titanium in niobium can also improve corrosion resistance, particularly in lower pH environments [2]. Titanium and zirconium also reduce the melting temperature of niobium and improve the ability of molybdenum to mix during melting. Because niobium and zirconium are closer in density to molybdenum, the last has a reduced tendency to segregate during melting [3]. Considering all factors mentioned above, the combination Ti-Zr-Mo with C can produce a hard, abrasion-resistant, inert, ceramic material.

Herein, thin Ti-Zr-Mo-C films have been deposited onto Si (100) substrates by direct-current magnetron sputtering and studied with respect to the stability of the structural and functional properties using the most commonly used methods.

The main experimental results of Ti-Zr-Mo-C films are: (1) stable Ti-C, Zr-C, Mo-C and C-C bonds are identified and the solid solution (Ti,Zr,Mo)C is formed, therefore, the film structure can be presented as the nanocrystals of above solid solution surrounded by a-C phase; (2) Knoop hardness steadily increased with increasing sputtering current at the graphite target to 250 mA reaching the maximum value of about 35 GPa; (3) the structure and properties of sputter-deposited metal carbide films are precisely controlled by composed with appropriate elements. The transition metals such as Zr and Mo have a strong effect on binary TiC films, due to their lower carbon affinity and their tendency to form complex crystal structures.

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Conference Track: “Multifunctional Thin Films & Coatings” 03mtfc-35
Non-Metal Interfaces in Superhard Nanocomposite Coatings: a First-Principles Study

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Abstract ID #MTFC-0321

Nanocomposite and nanolayered coatings are attracting attention due to their unique properties that are often superior to bulk parent materials. For example, these coatings exhibit an extreme hardness of 70–105 GPa, which is of the order of diamond [1].

In this presentation we will focus on analyzing the coatings that consist of the grain of transition metal compounds connected with non-metal interfaces. The properties of such coatings, to a great extent, are determined by their internal interfaces. However, a systematic analysis of the interfaces in these coatings and their impact on the properties has not yet been carried out. In this work, we give a review of the recent theoretical studies of the internal interfaces in nanocomposite and nanolayered coatings. The following systems were considered: MX/ SiY, M=transition metal, X, Y = C, N; MN/AlN, MN/BN, and TiB2/(BC, BN, AlN, SiC). The experimental results were comprehensively investigated, and the effect of interface structure on the mechanical properties was analyzed. Theoretical models of the heterostructures with one and several crystalline and amorphous interfacial layers were considered. The interfaces in nanocomposites can be dynamically and mechanically unstable due to lattice mismatches between the grain and interfacial materials. In this case, the amorphous interfaces will form. Otherwise, the epitaxial or hetero-epitaxial interfacial layers will form between constituent phases [2, 3]. This criterion is used to predict the temperature-induced structural transformation of the interfacial layers. Also, such an approach enabled one to explain the formation of the epitaxial interfaces with thickness less than 2-5 nm in a number of nanolayered coatings based on transition metal nitrides. An analysis of the stress-strain relations of different MX/SiY and MX/AlN heterostructures calculated in the framework of first-principles approaches showed that, with the electronic structure point of view, the strength properties (ideal tensile and shear strengths) of the nanocomposites and nanolaminates should be worse compared to those of the constituent transition metal compounds. So, the central role of the interfaces in the strength enhancement of nanocomposites is to impede the dislocation movement and crack propagation. It was also stressed that the blocking effects on the dislocation motions decrease with the transformation of the epitaxial or hetero-epitaxial layers into amorphous ones. Despite that, the amorphous phase can also act as an obstacle to dislocation movement, its impending effect on the dislocation motion is much smaller than that of a coherent interface. Therefore, the coatings with amorphous interfaces will exhibit lower hardness than those with epitaxial or hetero-epitaxial interfaces.

REFERENCES
WN/TiSiN Nanostructured Coating for Severe Tribological Applications

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The machining industry is well-known for the extreme conditions during processing materials that drastically limit the service life of the operating tools. Hard coatings are extensively employed to protect the surface of the expensive tools and reduce the usage of lubricants that can harm the environment. W-based coatings exhibited high hardness, low friction coefficient, and a self-lubrication effect due to the formation of oxides. Meanwhile, TiSiN coating is known for its high hardness due to the nanocomposite structure. Thus, a combination of WN and TiSiN in one multilayer architecture is expected to allow achieving a new coating with enhanced properties. The WN/TiSiN multilayer coatings were deposited by the cathodic-arc physical vapor deposition using upgraded “BULAT-6” equipment. The X6CrNiTi18-11 stainless steel was used as a substrate.

The total thickness was measured to be 4.2 μm, while thicknesses of individual WN and TiSiN layers were about 6.4 nm. Considering the features of the backscatter electron imaging, dark layers refer to the heavier element, which is WN, and brighter ones are TiSiN. The XRD analysis revealed that nanostructured WN/TiSiN coating consisted of the fcc NaCl-type W2N phase and fcc NaCl-type (Ti,Si)N solid solution. The nanohardness (H) and Young’s modulus (E), and elastic strain to failure (H/E ratio) were found to be 35.8 GPa, 431.7 ± 28.4 GPa GPa, and 0.083, respectively. The coating demonstrated enhanced hardness compared to the fcc-W2N and fcc-TiSiN, which can be explained by the multilayer architecture with various layers with different properties, Si addition, numerous interfaces between layers that hinder propagations of dislocations and cracks, the Hall-Petch strengthening due to the increased volume fraction of grain boundaries, and Koehler hardening that refers to the shear modulus differences between two different phases.

The wear behavior of the WN/TiSiN nanostructured coating was evaluated by two parameters: friction coefficient and specific wear rate. The steady-state value of the COF was measured to be around 0.51. The specific wear rate after sliding the counter-body Al2O3 ball against the surface of the multilayer was 5.2×10-6 mm3/Nm which can be considered as low wear. Therefore, WN/TiSiN coating demonstrated high hardness and elastic strain to failure, low friction coefficient, and wear rate. Such properties make the studied in the present work multilayer system a suitable candidate for extreme tribological applications with high temperature, pressure, and speed during the processing.

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Modification of the Inorganic-Organic Silica Coatings by Active Agents And its Influence on Long-Term Protection of P265GH Steel

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Corrosion is a worldwide major problem that is responsible for enormous financial losses and despite numerous attempts to create effective and durable prevention methods, still needs to be addressed [1]. One of the most commonly used methods to protect metallic substrate is to create a coating. Today’s science offers many different techniques to create coatings which successfully protect metallic surfaces [2]. Moreover, modern markets are advancing coating methods that not only guarantee efficient anti-corrosion protection but are also environmentally friendly. Hence such traits such as zero waste and being beneficial in terms of energy consumption are also factors necessary to consider when choosing a coating method process. Among “green methods” there is the sol-gel method, which gives the ability to obtain a product with controllable specific properties on a molecular level. Over the past years, improved control of the sol-gel process and further development of offered products triggered growth of the sol-gel coatings market [3]. Using the sol-gel method, it is possible to create various coatings providing long-term protection: by adding powders and nanopowders, nanocontainers, active polymers, etc [4]. Nowadays, the most successful sol-gel system for long-term protection consists of oxide sol-gel networks modified by active agents i.e., CeO₂ or ZrO₂ [1].

In this work, the silica sol-gel coatings based on 3-glycidoxypropylmethoxysilane (GPTMS), 3-aminopropyltriethoxysilane (ApTEOS), zirconium butoxide (ZrOBu) and active agents (Ce(NO₃)₃, CeO₂ and benzotriazole) are presented. Silica coatings on low carbon steel (P265GH) were tested for corrosion protection in 0.5M NaCl, ‘self-healing’ ability was examined by extending the time of exposure to corrosion agent (using EIS and LPR methods). Additionally, the SEM with EDX was used to characterize the morphology and chemical composition of coatings. The scratch test was conducted to determine mechanical properties like adhesion and friction.

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REFERENCES

Investigation of the Structure and Tribological Behaviour of Self-lubricating Magnetron Sputtered Mo-W-C Coatings

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In many industries, utilization of wear-resistant coatings is necessary for enhancement of lifetime, performance, and efficiency of moving contact parts. For these purposes, Diamond like carbon (DLC) coatings, usually prepared by magnetron sputtering or PE-CVD, offers very low coefficients of friction and wear rates [1]. However, the applications of Diamond-like carbon coatings are limited by the working temperature. If the temperature exceeds 400 °C, the coating is prone to graphitise, oxidise, and finally loses its excellent tribological properties. This drawback can be overcome by utilization of transition metal dichalcogenides, e.g. MoS2, and ternary metal oxides. However, these coatings do not keep their excellent wear resistance and low coefficient of friction across a wide temperature range [2]. The solution could be found by the application of self-lubricating Mo-W-C composite coatings with improved wear resistance under dry sliding conditions [3]. Such composite coatings containing solid lubricant phases usually offer good wear properties, lower coefficient of friction, and a wear surface with inhomogeneity at the nano scale level [4]. Based on above, the investigation of these coatings is the current state of the art [5]. The present research deals with the detailed study of the structure, phase composition, mechanical and wear properties of self-lubricating Mo-W-C coatings. The coatings were deposited on silicon substrates by the method of DC magnetron sputtering. The structure of the cross-sections of the coatings were investigated by high resolution scanning electron microscopy and atomic resolution transmission electron microscopy. The mechanical and wear properties of the coatings were studied using the nanoindentation and ball-on-disc method.

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Formation of Copper Coating on Polymer Granules by Chemical Method

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Abstract ID #MTFC-0383

All industries are constantly looking for new high-tech materials to improve the efficiency of products and mechanisms. Many materials that are based on polymers have a strength that is not inferior to the strength of some metals. However, their use for metal replacement is quite limited due to low thermal and electrical conductivity and some other properties. A number of properties of polymers can be significantly changed and improved by the use of fillers, in particular, the introduction of metals into the polymer matrix to create metal-filled polymer composites. Metal-filled polymer composites have significant potential for implementation in various industries.

Many methods of introducing a metal filler into the polymer matrix have been proposed. In addition to traditional and researched methods (melt and soluble mixing, in situ, polymerization filling, etc.), new methods are being developed to obtain high-tech polymer composites. We have proposed a technology that includes the formation of a layer of metal on the surface of the polymer raw material and the subsequent processing of such raw materials into products [1–4]. The result is to obtain a metal-filled polymer composite directly while forming the product.

Metal-filled polymer composites can also be used in areas such as catalysis. In this case, the catalytic properties of the material will be determined by the nature of the metal, as well as certain features of the surface structure. One of the most widely used metals as a catalyst is copper and its alloys. Thus, in addition to the traditional use of metal-filled polymer composites as structural and engineering materials, we can consider their use as a basis for creating catalytic systems in the processes of low-temperature production of certain substances.

We investigated the possibility of obtaining a copper coating on polymer granules by chemical methods as a result of the reduction of copper ions from solutions of its salts. Certain kinetic regularities of the process of copper layer formation on polymer granules have been established. The influence of the nature of the stabilizer of the chemical precipitation solution on the rate of reduction of copper ions and the duration of the induction period is investigated. It is shown that the crystal structure of the obtained copper coating does not depend on the composition of the used chemical precipitation solution. It was investigated by electron scanning microscopy that the surface morphology of the copper coating depends on the nature of the polymer on which the reduction of copper ions takes place. Such information can be the basis for the development of catalytic systems in which the formation of the appropriate surface structure of the copper layer will obtain the necessary catalytic properties.

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Elaboration of Epitaxial Rubidium Titanyl Phosphate Thin Films by Pulsed Laser Deposition

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The mm² orthorhombic potassium titanyl phosphate crystal, i.e. KTiOPO₄ (KTP), is a famous biaxial nonlinear optical crystal widely used commercially for second harmonic generation (SHG) or optical parametric oscillation (OPO) pumped by a 1.064 μm Nd:YAG laser for example. Most of its applications are based on bulk single KTP crystals. However, there is a strong interest to elaborate submicrometric waveguides in the framework of integrated photonic devices. Among several waveguide-fabrication techniques such as proton exchange, ion implantation or dicing [1], a serious alternative is Pulsed Laser Deposition (PLD). Indeed, it was reported that type-II second-harmonic generation and sum-frequency mixing could be realized in uniform epitaxial RbTiOPO₄ (RTP) films over KTP channel waveguides prepared by PLD [2]. Such waveguides could be a serious alternative to efficient low energy nonlinear optical devices in particular for Telecom or spectroscopic applications.

PLD is a technique particularly well suited for growing single oxides films with complex chemical composition. This technique consists in a high energy laser ablation of a material with the same chemical composition than that of the desired layer. The plasma of the ablated material is then condensed on the substrate and heated to a temperature such as the aggregates can self-organise on the atomic lattice of the substrate leading to the epitaxial layer.

In this study, we performed epitaxial growth of the RTP phase on KTP single crystals by PLD. The target that has been used was a single RTP crystal. Thanks to combined microscopies (SEM, AFM, TEM) and diffraction (X-ray, electron), we investigated the effect of the deposition parameters (PO₂, Temperature, laser fluence) on the growth rate, as well as the morphology and crystal structure of the layer.

We were able to determine the conditions leading to the growth of an epitaxial layer of about 100 nm. We also observed that the crystallographic orientation of the substrate has a strong influence on the quality of the obtained layer. The choice of the deposition face is then of prime importance. Actually, we demonstrated that the natural face (100) gave rise to the most satisfactory growth.

REFERENCES


Study of Physical and Mechanical Properties of High-Entropy Alloys by Machine Learning Methods

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Taking into account the latest studies over 20 years, the scientific direction of the fields ranging from statistics and mathematics to the study of quantum phenomena can be confidently claimed to be a scientific breakthrough. Most of these areas, taking into account only those that indirectly or directly relate to the fields of nanotechnology, materials science, and metallurgy, require the study of new materials. Given the difficulty in fabrication and insufficient information about the formation of high-entropy alloys in practice, we decided to integrate machine learning principles to predict this type of alloy [1].

Today there are a large number of solutions for modelling and research of material parameters. Thanks to such solutions, there are opportunities to study the modulus of elasticity, and hardness [2]. Among the most common and considered methods, for high-entropy alloys study the following most successful methods were singled out: (i) simple linear regression methods; (II) the method of «random forests»; (iii) gradient boosting method.

The boosting method is a powerful algorithm that combines several basic classifiers to create an ensemble of predictors with better performance than using other basic algorithms with classifiers. The main idea of boosting is that a new model is superimposed on each successive ensemble of predictors. At each new iteration, weak inaccuracy or other chosen parameter to determine the correctness of the imaginary branch of the tree learns about the errors of its ensemble of predictors, mastered at the moment, when like many other methods can not correct their errors in gradual iterations. This allows you to increase the accuracy of prediction by the method of the results of the previously specified functions [3].

The purpose of this work is to test the selected algorithm based on data taken from open databases, such as a material project. Created based on linear regression, artificial intelligence should use the transfer type of learning, with its subsequent adaptation to the physical-mechanical model. To implement, you need to use open modules created in the python programming language. It should be noted that the fewer elements, the more accurately determine the physical and mechanical properties of the alloy. The ability to combine materials into one link will also play a role.

The main method of research is the regressive method of random forest regressor and its improved version of gradient boosting. In this case, the method uses and takes information from open and sorted databases. Statistical analysis required a lot of calculations, especially in our case, when the alloy is highly entropic. For a more specific test, a Vickers hardness study can be performed in practice. Obtained data allowed us to characterize the brittleness, shear, and deformation modules and the generation of formation and generation of new alloys of different types of structures.

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Study of the Microstructure and Mechanical Properties of Wire and Arc Additive Manufactured 5087 Aluminium Alloy

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Wire and Arc Additive Manufacturing (WAAM) has unique advantages in terms of welding efficiency and manufacturing costs. The mentioned technology is ideal to produce dimensional components with a surface condition almost identical to the “final shape” already after the WAAM process itself [1-5]. The goal of the paper was the production of two walls using MIG pulse based WAAM and analysis of their properties. A 20 mm thick sheet of AW5083 aluminium alloy was used as the base material, and a wire with a diameter of 1.2 mm made of 5087 aluminium alloy was used as the filler material. Before additive manufacturing the walls themselves, 6 single-layer overlay welds were deposited to determine the optimal welding parameters. Two set of welding parameters were selected. Before deposition of the walls, the base material was preheated to a temperature of 350 °C. The filler wire feed rate used for production of the first wall was 4.5 m/min, the welding speed was 5 mm/s and the heat input was 183 J/mm. Produced wall consisted of 43 tracks with a total height of 89 mm and an average width of 8.7 mm. The filler wire feed rate used for production of next wall was 5.5 m/min and the calculated heat input was 265 J/mm. Wall No. 2 consisted of 46 tracks with a total height of 89 mm and an average width of 11.6 mm. The increase in heat input caused an increase in the width of the weld and the depth of the weld. Microstructural analysis demonstrated that the heat affected zone of both walls exhibits a refined polyhedral structure with secondary phases precipitated along the grain boundaries. The weld metal has a dendritic morphology in the volume, in the region adjacent to the heat affected zone it is a columnar dendritic morphology, and there are pores present in the structure. The dendrites are formed by α solid solution and secondary phases, such as Al\(_3\)Mg\(_2\), that are precipitated in the interdendritic spaces. Microhardness measurement showed that the average microhardness of the weld metal of wall No. 1 showed a value of 71.5 HV0.1 and for wall No. 2 a value of 78.0 HV0.1 was measured. It was shown that the microhardness of the weld metal was lower than that of the base material.

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Electrophoretic Deposited Graphene Quantum Dots and Ti$_3$C$_2$-MXene Thin Films for Electrochemical Detection of Neuron-specific Enolase

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The detection of cancer-specific biomarkers is reported as an efficient remedy for early diagnosis. In the present study, we report the results of the studies related to the development of Ti$_3$C$_2$-MXene and graphene quantum dots (GQDs) nanohybrid based label-free electrochemical biosensing platform for neuron specific enolase (NSE) detection. The synthesized amino-GQDs@Ti$_3$C$_2$-MXene nanohybrid is characterized by different analytical techniques. Following that, the electrophoretic deposition (EPD) technique is employed for depositing the thin films of GQDs@Ti$_3$C$_2$-MXene nanohybrid on indium tin oxide (ITO) coated glass substrate. Monoclonal antibodies (anti-NSE) are covalently immobilized to amino-GQDs@Ti$_3$C$_2$-MXene/ITO electrode using EDC-NHS chemistry and bovine serum albumin (BSA) is used for blocking the nonspecific binding sites. Further, the electrochemical response of anti-NSE/amino-GQDs@Ti$_3$C$_2$-MXene/ITO immuno electrode is recorded with different concentrations of NSE biomarker in standard and spiked serum samples using differential pulse voltammetry (DPV) technique.
Electronic and Thermal Properties of Ti$_3$C$_2$-MXenes for Sensing Applications

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MXenes are a new family of two-dimensional (2D) nanomaterials exhibiting extraordinary physical properties and attracting much interest of researchers with respect to their possible applications. In this work Ti$_3$C$_2$-MXene materials obtained from Ti$_3$AlC$_2$ MAX-phase precursor from different preparation routes have been studied. They have been thoroughly characterized with temperature dependent XRD, TGA/DSC, EDS-SEM and their electrical and thermal properties have been investigated in a broad temperature range from 300 K down to 3 K. Measurements of the electrical resistivity, Seebeck coefficient, thermal conductivity and specific heat have been carried out. The experimental results were supported with theoretical calculations of the electronic structure and related physical properties.

The low temperature specific heat data show a linear dependence corresponding to a finite density of states at the Fermi level. They also reveal a low value of the Debye temperature of 170 K. This is consistent with the calculated densities of states. The character of the DOS at the Fermi level is correlated with the negative sign of the magnetoresistance in the materials and is compared with those in the related MAX phase. The results obtained on the properties of the materials studied are analyzed and considered with respect to low temperature sensing and possible space applications.
Low Temperature Alternatives for Reactive Sputtering High Quality Stoichiometric Metal Nitride Films

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In this presentation, we will compare different reactive sputtering processes for the deposition of various metal nitride films at room temperature. The first half of this talk will cover how we produce high optical quality silicon nitride films using a low temperature reactive sputtering method that includes a combination of remote radio-frequency inductively coupled plasma (RF-ICP) and substrate biasing. Both the RF-ICP source and the biasing of the substrate create a plasma consisting of low-energy ions and excited atoms of gases, providing films with increased material reactivity without the need of actively heating the substrates.

In the second part of the presentation, we will discuss reactive bipolar HiPIMS as an alternative process to obtain dense, stoichiometric titanium nitride (TiN) films with promising superconducting properties at room temperature. The TiN films obtained using this new approach were highly dense, stoichiometric, pure, and demonstrated favorable superconducting properties. The bipolar HiPIMS process is a valid alternative to many reactive nitride processes that typically require high temperatures, biasing, and/or remote plasma assist.
Effect of Pr and Er Additives on Mg-based Alloy Structure Prepared via Mechanical Alloying

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The aim of this work is to define how different rare earth metals alloying additions, namely erbium and praseodymium differ in terms of effect on the particle size, morphology and phase composition on magnesium-based alloys prepared via high energy mechanical alloying. Within the structure characterization, the effects of milling on particle size, morphology, amorphousness, and phase composition were investigated. Three sets of samples for each element, varying with the REE content from 1 to 3 at.%. Every set was milled for 20 cycles. The results showed that the particle size decreased along with higher REE content. Moreover, the samples containing erbium featured much smaller particle size as compared to those with praseodymium. The mass median diameter (D50) of each sample were 34.69, 31.14 and 29.43 µm for Pr and 19.81, 17.67 and 14.65 µm for Er, respectively. Moreover, the XRD analysis revealed amorphous traits with varying degree in all samples, along with MgZn2 phase. SEM investigation revealed homogeneous distribution in the samples for Er, however in case of Pr some clusters of unreacted Pr remained. In conclusion Er addition decreases the size of the powder particles, thus making it beneficial for consolidation, on the other hand Pr reacts in worse manner during mechanical synthesis.

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Structure Characterization of Mg-Zn-Ca Alloys with Au and Ag Addition

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The aim of this work was to present a structure and morphology analysis of a powder of Mg-based alloy with noble metal additives. The Mg_{66-x}Zn_{30}Ca_{4}Au_{x}/Ag_{x} (where x = 1, 2 at. %, samples were named accordingly to the addition content Au1, Au2, Ag1, Ag2) alloys were obtained via high-energy mechanical alloying, for 50 and 70 h of milling. The research encompassed structural and chemical analysis, phase composition and laser size particle measurement, as well as Vickers microhardness. The results indicate a presence of similar phases in all samples, mainly MgZn_{2}, Zn and Mg, with a difference of the AuZn_{3} phase in Au-containing samples. Amorphous phase was present mainly in Ag1 and Ag2 samples. In samples containing Au1 and Au2 amorphous phase is present along nanocrystalline phases. SEM and EDS analyses revealed homogeneous distribution and chemical composition consistent with the base material. The average particle size (D50) in samples milled for 70 h were 22, 28, 29 and 35 μm for Au1, Au2, Ag1 and Ag2 alloy respectively. The particle size increases along with the noble metal content, independently of the milling time. Similar tendency has been observed in samples after 50 h. The hardness measurement was carried out at 50 gf load (HV0.05) and dwell time 15 s. The microhardness analysis for alloy after 50 h milling results of Au1, Au2, Ag1, Ag2 alloys were 318, 308, 315, 352 HV0.05 respectively. However microhardness analysis for alloy after 70 h milling Au1, Au2, Ag1, Ag2 alloys were 333, 264, 264, 422 HV0.05 respectively. Concluding the results, Ag addition seem to increase the hardness of the sample along with the alloying element content, whereas Au decreases.

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TRACK 4
“NANOSCALE CHARACTERIZATION & IMAGING”
Insight into the Diffusion of Electrically Active and Inactive Impurities

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Precise and reliable determination of the spatial distribution of dopants in the structure, as well as prediction of its temperature behavior, is crucial for the practical applications of semiconductors. Standard dynamic Secondary Ion Mass Spectrometry (SIMS) provides depth profiles of impurity atoms without distinguishing electrically active and inactive parts. In contrast, Electrochemical Capacitance -Voltage (ECV) technique yields depth profiles of all carriers present in the structure. Observing significant discrepancies between the profiles measured by these two techniques, which exceeds their measurement uncertainty, sparks the discussion on the varying diffusion of electrically active and inactive impurities.

In our research, we aim to show a clear distinction between diffusion rates of total and electrically active impurities for various doped III-V structures. The initial ECV and SIMS experiments suggest that the total impurity distribution extends substantially deeper than its electrically active part. Furthermore, the results imply higher mobility of inactive impurities under thermal treatment that presumably can move interstitially. In the first experiment, we investigated the Si-doped GaAs layer of 500 nm thickness embedded between undoped GaAs layers (GaAs/GaAs: Si/GaAs). Samples subjected to thermal treatment at a temperature range of 800–1000 °C for 30 minutes were tested using SIMS and ECV techniques, which will provide data for the quantitative determination of the diffusion parameters of the active and total impurity giving a starting point for a discussion on the diffusion mechanisms. The proposed complementary use of SIMS and ECV techniques shows a great promise to be a highly beneficial tool in optimizing growth processes, determining the cause of electrical inactivity, and controlling the level of dopant activation in ultra-thin structures.

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Secondary Ion Mass Spectrometry
Quantification of Boron Distribution in Silicon Nanowires

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The secondary ion mass spectrometry (SIMS) technique has been used to quantify dopant distribution in electronic materials for decades. However, the classical approach, one-dimensional depth profiling, cannot directly applied to analyze non-planar transistors like fin field-effect transistors and the gate-all-around field-effect transistors (GAAFET). Even though many SIMS instruments are equipped with position-sensitive detectors, the ion bombardment of the three-dimensional structure leads to non-uniform and impossible to predict sputtering process.

In this work, we show how to perform SIMS measurements on silicon nanowires (NWs) which can be further processed into GAAFET devices. Before the measurement, the structure is embedded in an organic matrix to ensure that NWs are sputtered from the top and not from aside. However, for standard measurement conditions, the sputtering rate of the organic material is more than an order of magnitude higher than that of the silicon which impedes the analysis. Application of high incident-angle ion bombardment practically eliminates this difference and a sample can be uniformly sputtered and boron distribution along NWs can be quantified.

The analysis has been performed on an array of 100 x 100 boron-doped silicon NWs which were subjected to various oxidation processes followed by oxide removal. SIMS analysis confirms the segregation of boron towards the oxide and its depletion from the cores of nanowires. The results are in line with TCAD 3D simulations. Moreover, the intensity of the silicon signal scales linearly with the area of NWs and thus their diameter can be determined directly from the SIMS measurement, which proves the stability of the proposed measurement procedure.

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Existence of Gaseous Nanodomains on Graphite Surface as a Consequence of Its Aging

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Abstract ID #NCI-0059

Although graphite is often regarded as a relatively inert material, changes between freshly exfoliated HOPG and surface aged by exposure to ambient air are reported [1, 2]. So-called aging of solid surfaces is ascribed to deposition of airborne carbonaceous contaminants upon relatively short (minutes) exposition to ambient atmosphere, which leads to surface hydrophobization [3].

Compared to a freshly prepared surface, which is fully wetted, ambient gaseous nanodomains are spontaneously formed on aged basal plane HOPG surface upon its immersion in water. This behavior is explained by the entrapment of ambient gas dragged into water upon surface immersion and by forming surface gaseous nanopockets due to incomplete wetting of the hydrophobized surface. To the best of our knowledge, this is the first study of the direct relations between the aging of carbon-based materials and the apparent density of gaseous nanodomains on its water-immersed surface.

The work addresses broader aspects of this phenomenon: Gaseous nanodomains can cover a significant fraction of immersed (aged) graphite surface, cutting down the effective area of the solid-liquid interface. Aging may thus affect the utilization of graphite as a material for electrochemistry and other processes at the solid-liquid interface. In general, it may have a deteriorating effect on processes, which efficiency relies on the area of the solid-liquid interface. As immersion of solids into the liquid phase represents an initial step of all processes taking place at the solid-liquid interface, understanding the mechanism of this phenomenon has high importance.

REFERENCES


Nanostructure Characterization and Film Thickness Measurements at the Fabrication Line

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Abstract ID #NCI-0061

Roll-to-roll embossing is a fast and relatively inexpensive method for producing nano-textured polymer foils in high volumes. This is done by pressing a stamp mounted on a roll into a moving polymer film at elevated temperature. We present results from an optical scatterometric method for characterizing the dimensions of roll-to-roll embossed periodic nano-grating surface structures, which give rise to optical colour effects. The characterization method is based on a hyperspectral line scan camera, which provides images with high spectral resolution at high framerates. Feature heights are extracted with nm resolution by comparing the measured transmission spectra with simulations performed using the rigorous coupled-wave analysis (RCWA) method [1]. This enables the operator to optimize fabrication parameters such as roll speed, temperature and roll pressure in real time during fabrication by performing in-line, non-destructive quality control [2]. The imaging capabilities of the employed camera provides an overview of the embossed foil, allowing the operator to choose areas for analysis during- or after production.

In the present work, data is presented for sinusoidal and square type gratings printed on Poly Carbonate (PC), Polyethylene (PET), and polymethylmethacrylate (PMMA). A computer algorithm for automatically identifying areas of interest based on the imaging data from the hyperspectral camera is employed. Further, it is demonstrated that film thicknesses can be determined by analysing the interference pattern observed in the spectrum of white light transmitted through thin polymer films.

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REFERENCES

Application of Stable Isotopes in Probing at Nanoworld

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Stable isotopes, such as $^{18}$O or deuterium, are undermined in surface engineering topics. Yet, they are very powerful species in probing materials to identify and track ions diffusion at the nanoscale under various technological conditions. The isotopes act as tracers and markers, which can be traced ex-situ by application of sensitive isotopic techniques, among which a family of ion beam analytical methods is most powerful. The concept of ion beam analysis (IBA) of markers or tracers in studying diffusion in solids, permeation phenomena, or plastic deformation is known. However, it is not widely used due to some practical challenges, which will be discussed. IBA, or more precisely, the family of ion back-scattering and nuclear reaction methods, has been well established in experimental nuclear physics over the past 70 years. There have been extensively used in Si technology since the early 70s of the XX century. On the other hand, nanoporous oxides on Al and other important metals and their alloys such as Ti or Zr continuously receive interest from many branches of nanotechnology, batteries, supercapacitors industry, and corrosion science. The ultimate goal is to form a tailored, highly ordered nanoporous oxide film on a large scale by electrochemical methods, much cheaper than photolithography. Thus, understanding interdependencies and mastering the parameters leading to the formation of higher-order porosity is key to achieving it. The film is formed due to inward migration of oxygen and outward migration of Al under the electric field above the critical value allowing the transport and, most likely, plasticization and flow of the alumina under the mechanical stress. The exact mechanism of the alumina formation during the anodizing process is not fully understood yet, with very little work done on the movements of oxygen or hydrogen, which is present in the film.

This paper aims to present the practical application of the tracer/marker tracer approach in combination with accelerator-based techniques, the unique features of the methodology, and present to the reader complementary techniques, which, with some careful pre-testing and planning, can be successfully applied instead of IBA. The examples used here are limited to the investigation of thin oxide films on light metals [1, 2], but the marker/tracer concept can be easily implemented to study other thin film materials at the nanoscale [3, 4]. A comparison was made between plasma profiling time-of-flight mass spectrometry (PP-TOFMS), nuclear reaction analysis (NRA), and Narrow Resonance Depth Profiling (NRDP) of 18O tracer in alumina. The findings from PP-TOFMS revealed a partitioning of the tracer between the surface regions and buried layers of the films, in agreement with the NRDP. It demonstrated a level of complementarity of PP-TOFMS and potentially becoming a faster method for 18O depth profiling than NRDP.

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Particle-by-Particle Mapping by Fluorescence Microscopy: Characterizing the Surface Composition and Subpopulation Heterogeneity of Bionanocomposites

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There is great optimism that nanomedicine holds the potential to revolutionize the diagnosis and treatment of disease. The integration of nanotechnology in medicine has seen the emergence of a range of bionanocomposite materials, which may be spontaneously or synthetically derived. We believe that the biological recognition and behaviour of these bionanocomposites is, in part, controlled by the precise composition of their surface biomolecular architecture.[1, 2] The biomolecular architecture, adsorbed or conjugated on the nanomaterial surface, constitutes a major element of the bionanocomposite’s biological identity, mediating interactions with cells and biological barriers.[3, 4] Gaining a comprehensive understanding of bionanocomposite surface composition is challenged however by a lack of techniques capable of characterizing the biomolecular architecture in situ, directly on the nanomaterial surface, on a particle-by-particle basis. In particular, since analysis is typically performed on the bulk suspension rather than on individual particles, current characterization strategies provide only a generalized interpretation of bionanocomposite surface composition, describing key attributes with averaged values. This one-size-fits-all approach is wholly inappropriate, as it conceals the true nature of the collective suspension, which will be comprised of a heterogenous mixture of states.

Here, we introduce a characterization strategy based on confocal laser scanning microscopy, which permits in situ evaluation of bionanocomposite surface composition on a particle-by-particle basis. The technique relies on the incorporation of fluorescent tags into proteins of interest prior to preparation of the bionanocomposite, to enable tracking of the protein’s integration within the surface architecture. Confocal laser scanning microscopy allows for the visualisation of individual fluorescent nanoparticles, and thus, on a particle-by-particle basis, determination as to whether or not the protein of interest has been incorporated within the bionanocomposite surface architecture. In conjunction with analytical image processing software, the strategy allows for the characterization of thousands of particles, providing statistically robust results. The technique may be complemented through the use of external fluorescent immunolabels, which probe the presence of both the protein and incorporated fluorescent tag on the nanomaterial surface. In addition to acting as a means of validation, this external immunolabelling provides further information as to the surface accessibility of key proteins, which is central to the cellular recognition and interactions of the bionanocomposite. We demonstrate the utility of this fluorescence mapping strategy in characterizing the surface composition of bionanocomposites, highlighting it’s potential to unveil heterogeneities in the biomolecular architecture and to identify distinct subpopulations within the suspension.

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Sub-Monolayer Coatings of Molybdenum Oxide Used for Relative Sensitivity Factors Determination in “Storing Matter” Secondary Ion Mass Spectrometry

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In this work, we present how sub-monolayer molybdenum oxide coatings are used for determination of relative sensitivity factors (RSF) of storing matter (SM) technique applied to secondary ion mass spectrometry (SIMS) analytical method [1, 2]. The SM technique enables quantitative analysis of SIMS by separating sputtering process and process of secondary ion formation. In this technique, the sputtered material of ion bombarded surface is deposited onto the substrate so as to obtain a coating with a thickness of less than one atomic layer. Then, the substrate with the stored material is analysed using the classical SIMS analytical method.

A series of 20 pure elements were studied with the SM technique. As substrates we use 300 nm thick molybdenum oxide MoO3-x layers deposited onto titanium plates by vacuum evaporation of ultra-pure MoO3. The experiments were carried out on the Hiden SIMS Workstation apparatus equipped with a special sample manipulator enabling positioning of samples for sputter deposition process and for the analysis of the deposited material.

A beam of 5 keV, 48 nA O2+ scanned over 600 x 600 µm area was used for sputter deposition of sub-monolayer deposits onto MoO3-x substrate, and the same beam scanned over 3000 x 3000 µm area was used for the SIMS analysis of the deposit.

The obtained results of each of the 20 measured elements allowed to calculate the RSF factors and plot them versus atomic mass, as well as versus first ionization potential values of the examined elements. The plots were then compared with the plots of typical SIMS RSF factors and also with RSF plots of glow discharge mass spectrometry (GDMS) [3] - another analytical technique. The results show how SM SIMS RSF factors differ from classical SIMS technique values and how they approach the GDMS RSF values.

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Surface Morphology of Metallic Nanolayers: Thickness & Substrate Dependence

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Downgrading the size of electronic devices requires extending the knowledge about the properties of materials on the nanoscale. Experimental research in the nanoscale is indispensable due to the difference in nanomaterials and bulk materials features, e.g., semiconductor-like properties of Au films under a certain thickness (~5 nm). These differences arise from the quantum and surface effects that have a negligible impact on the bulk structures [1]. The surface effects of nanolayered materials are strictly associated with the overall thickness of the nanolayers and the type of substrate on which they are deposited.

In this work, surface characteristics of metallic nanolayers were compared in the dependence of the layer thickness and the type of substrate. The nanolayers were deposited on Topsis (Warsaw, Poland) Si (100) polished prime wafers type N obtained using the CZ method and Si (111) and SiO2 wafers obtained by the hydrothermal crystallization. Deposition of metallic nanolayers of various thicknesses was carried out at the Institute of Microelectronics and Photonics (Warsaw, Poland). The topographical properties of the nanolayer surface were investigated using a scanning tunneling microscope (Institute of Physics, Jan Kochanowski University, Kielce, Poland).

The STM measurements of the studied samples were performed using SPM Aarhus 150 (SPECS & University of Aarhus), ensuring outstanding stability gained from the miniaturized approach mechanical loop between sensor and surface. Operation with Nanonis control system (SPECS Zurich) allows for highly advanced control of electronic devices and the feedback control system during the scan to compensate for hysteresis or thermal drift distortions. The tip was polycrystalline tungsten wire etched by the argon ion sputtering in situ [2]. Measurements were performed in the ultra-high vacuum chamber (10−10 mbar) at room temperature.

The obtained images were analyzed with the WSxM, a freeware SPM software [3] for data acquisition and processing. Checking the authenticity of the obtained images was determined by confirming the correctness of the profile mapping during the trace and retrace scan directions, as well as by repeatability of the occurring structures in subsequent scans. The collected data made it possible to compare surface properties, e.g., average roughness of the nanolayers with different thicknesses and deposited on different substrates.

REFERENCES

Optical and Electron Microscopy Studies of \( \text{Al}_2\text{O}_3 \) Nanomatrices with Embedded ADP and KB5 Nanocrystals

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This paper studied the optical and electron microscopic characteristics of \( \text{Al}_2\text{O}_3 \) nanomatrices with different pore diameters with inclusions in the pores of ammonium dehydrophosphate crystals (ADP). The nanopores of \( \text{Al}_2\text{O}_3 \) matrices were filled with the ADP crystals, molecular formula \( \text{NH}_4\text{H}_2\text{PO}_4 \), according to the method described in [1-2]. Optical characteristics were studied in the wavelength range of 1-10 \( \mu \)m. It is established that the reflection coefficient in the investigated range for some samples \( R \leq 1 \). The low reflection coefficient value can be due to diffuse light scattering and the low refractive index of \( \text{Al}_2\text{O}_3 \) nanomatrices with the inclusion of ADP crystals. In order to assess the influence of the surface of the studied samples on the value of the reflection coefficient, electron microscopic studies of the surfaces of these samples were performed. From the conducted electron microscopic research, it is difficult to establish the reason for the reflection coefficient \( R \) behavior in the investigated range of wavelengths. To establish the reasons for the behavior of the reflection coefficient \( R \) in the studied wavelength range, an additional set of experiments on the study of \( \text{Al}_2\text{O}_3 \) nanomatrices with inclusions of ADP crystals has been proposed.

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REFERENCES


Tuning the Structural and Electronic Properties of TiO$_2$(110) Surface via Repeated Sputtering and Annealing

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Titanium dioxide is undoubtedly one of the most studied transition metal oxides. This material, also in its crystal form, has a wide variety of applications ranging from photocatalysis, solar cells, memristors, sensors to antibacterial films. However, in order to optimize its properties for subsequent applications in device design, it is important to know the properties of its surface. Hence, a relatively simple model system is essential to understand and improve the system under study. In order to study surface processes, a well-defined, clean monocrystalline surface is necessary, and various methods are known to obtain such a system.

In the talk we will concentrate on standard “cleaning procedure” composed of repeated sputtering and annealing cycles, leading to a clean, crystallographic surface, with well-defined terraces. However, both processes, sputtering and annealing, when used separately, are processes that lead to a reduction of the surface of oxide materials and by changing its stoichiometry lead to a modification of its physicochemical properties. The aim of our study is to investigate how these two processes, when used together, affect the electronic properties of the surface and subsurface regions on the nanometer scale. We will show how different might be the properties of the model system depending on the way it is prepared, i.e., how many cycles the surface underwent [1]. For this purpose, local microscopy methods (Kelvin probe force microscopy and atomic force microscopy with local conductivity) working in the ultrahigh vacuum conditions were used. Our study clearly indicates that cleaning cycles affect the electronic properties of TiO$_2$ surfaces, and that both sputtering and annealing can be used as methods to alter and tailor these properties depending on the required performance.

REFERENCES

Transformation of Nanopores in the MgO-Al2O3 Ceramics under Influence of Water

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Abstract ID #NCI- 0393

Humidity-sensitive elements based on nanostructured spinel MgO-Al2O3 ceramics are actively used in sensor electronics due to their ease of production, flexibility and stability of performance [1]. However, to obtain a material with predetermined properties, it is necessary to optimize the technological conditions for obtaining the structure of the main components (grains, grain boundaries, pores), which would maximize the adsorption and desorption of water and be resistant to other external factors [2].

The goal of this work is investigation of the evolution of extended defects as well as nanopores in the MgO-Al2O3 ceramics prepared at 1300 °C for 2h at influence of water and microstructural properties and phase composition of ceramics.

Extended free-volume defects and evolution of nanopores at adsorption were investigated by PALS method using an ORTEC spectrometer. The researches were made for the initials samples of ceramics and after placing the samples in water for 12 h. Due to the details of the experiment, the obtained PALS spectra were analyzed by the LT computer program at decomposition into three components.

It is shown that microstructure, phase composition, features of pore size distribution of nanoporous MgO-Al2O3 ceramics prepared at 1300 °C for 2h - humidity-sensitive material for active elements of sensor electronics were studied. It is shown that studied ceramics is described by developed structure of grains, grain boundaries with extracted edition phase and pores with different shapes and sizes. The investigated ceramics are two-phase, contains main phase of spinel and addition MgO phase. The porous structure of ceramics is described by the trimodal pore size distribution. In the study by PALS method it was shown that the presence of water in ceramics leads to the increase of positron trapping rate in defects, their slight expansion. The size of the nanopores was estimated by the lifetime of the third component according to the Tao-Eldrup model. It was shown that the adsorption of the adsorption of water by ceramics leads to the fragmentation of free volume in nanopores. The value of lifetime of the third component off 1.88 ns in water-immersed ceramics also indicates the o-Ps decay in water.

REFERENCES
TRACK 5
“NANOPHOTONICS”
Cuprates Nanowires for Superconducting Nanowire Single Photon Detectors

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Superconducting nanowire single photon detectors (SNSPDs) have shown unparalleled performance from the telecommunication wavelength down to 10 μm, including high quantum efficiency, high operating frequency, low dark count rate and low jitter [1]. Thus, SNSPDs are particularly suitable for quantum optical requirements and deep space-to-earth communication applications, among others. Their main drawback is their operating temperature well below 4 K since they are most often fabricated with low temperature superconducting thin films such as Nb or NbN. Indeed, they require complex cryogenics which limits the technological applications. For this reason, it is desirable to implement such detectors using high temperature superconducting (HTS) materials. However, this remains very difficult as the superconducting properties of HTS thin films are very sensitive to the nano-patterning process, generating oxygen diffusion and defects.

In YBa₂Cu₃O₇₋ₓ (YBCO) nanowires [2] fabricated by electron beam lithography and high-energy ion implantation, DC measurements demonstrate that the superconducting properties of the nanowires, in particular their critical current densities (jC) and critical temperatures (CT), are preserved compared to the bulk YBCO thin film. A large hysteresis in the IV characteristic is a common feature of low-temperature SNSPDs that is an essential condition for the creation of hot spots in SNSPDs. However, so far, no photoresponse has been reported despite the best efforts of groups around the world. This can be attributed to the fact that the thickness of the nanowires is too great.

To achieve single-photon photoresponse and sensitivity in a cuprate nanowire, the next step is to reduce the thickness of the superconductor to approach that of 2D materials. This leads to a superconductor-insulator transition (SIT). A new method presented here allows us to fabricate Bi₂Sr₂CaCu₂O₈₊x (BSCCO) nanowires whose superconducting properties can be tuned by field effect. Using the previously reported anodic bonding technique combined with exfoliation [3-5], we obtain very thin layers of high quality 2D superconductor. The fabrication of atomic layer nanowires is explored on pre-modeled soda-lime glass (SLG) substrates.

REFERENCES

Features of Cyanine Dyes J-Aggregates Formation on TiO₂ Matrices

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Under certain conditions, the molecules of some dyes and pigments can form highly ordered structures (molecule aggregates). Due to the translational symmetry of the molecules inside such aggregates, the electronic excitations of individual molecules are delocalized over the segments of chains of aggregates with the formation of Frenkel exciton. Depending on the arrangement of molecules in the chain, the exciton band can be narrow, strongly redshifted (J-band), or broad, blue-shifted (H-band) [1]. An urgent problem is the creation of solid samples of J-aggregates with higher photo- and physical stability compared to solutions. Such samples can be obtained, for example, in the form of polymer films or porous matrices. For example, porous titanium dioxide is an attractive material due to its high stability, excellent electron transport properties, and ability to control surface morphology [2].

In this work, the features of some cyanine dyes aggregation in TiO₂ matrices formed by different methods are shown. For all J-aggregates, a broadening of the exciton bands was found, demonstrating typically with Stokes shifts increasing. Using J-aggregates of pseudoisocyanine (PIC) dye the difference between formation on microcrystalline and nanocrystalline TiO₂ matrices has been demonstrated. As another possibility to influence the cyanine dye aggregation, the preparation of TiO₂ matrices from differently charged TiO₂ nanocrystals has been proposed.

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REFERENCES

Influence of Solid State Phases Interaction on Optical Properties of Oxide Glass-Ceramics Nanocomposites

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Abstract ID #N-P-0113

Materials composed of amorphous (matrix) and crystalline (filler) components, called glass-ceramics (GC) composites, can reveal improved characteristics or even new properties compared to starting components. Those peculiarities and their contribution to macro-characteristics of composite materials are determined by the interaction between amorphous media and crystalline particles incorporated. This interaction is determined by the charges, the degree of the electron shells overlapping, the mutual diffusion of atoms and molecules located at contacting surfaces of the matrix and filler, etc. As a result, interphase transitional layers are formed between matrix and particles, and the properties of these layers differ from the properties and characteristics of initials components. The role of such transition layers should increase if the incorporated crystal particles are nanosized, in other words, if you are dealing with nanocomposites. Suppose one finds correlations between the composition and structure of the original components and between the conditions of formation and new characteristics of the composite. In that case, you can suggest ways to control its properties. Thus, you get the opportunity to perform engineering of glass-ceramic composites and achieve the characteristics required for certain applications. E.g. in this way, you can try to get optical glass-ceramic materials with characteristics optimal for use as fluorescent coatings of base violet or blue LEDs. Such layers transforms a base LED into white LEDs (WLEDs).

Today, luminescent coatings made on the basis of polymer matrices are used in the production of WLEDs, which makes such coatings and, of course, which makes such FF, and just WLED short-lived.

In this work we present a short literature data review concerning the main approaches in the study of interphase transitional layers, especially those that concern inorganic systems and oxide systems are among them. Own experimental and theoretical (computer simulation) results were also discussed. We studied glasses made on the base of glass forming B\textsubscript{2}O\textsubscript{3}, P\textsubscript{2}O\textsubscript{5}, V\textsubscript{2}O\textsubscript{5} and modifying MoO\textsubscript{3}, WO\textsubscript{3}, and Bi\textsubscript{2}O\textsubscript{3} oxides. These glasses were incorporated with nanocrystalline particles of complex oxides such as KBi(MoO\textsubscript{4})\textsubscript{2}, K\textsubscript{2}Eu(PO\textsubscript{4})(WO\textsubscript{4}), KBi\textsubscript{1-x}Pr\textsubscript{x}(MoO\textsubscript{4})\textsubscript{2}, La\textsubscript{1-x}(Eu/Sm)\textsubscript{x}V\textsubscript{O\textsubscript{4}}, etc. The GC samples were characterized using powder X-ray diffraction, differential thermogravimetric analysis (DTA), scanning electron and atomic force microscopy, absorption, IR, and luminescence spectroscopy. Theoretical (computational) study of the spatial and electronic structures of interphases in various types of composites were performed, too. The ways of some glass-ceramics nanocomposites optical properties "engineering" will be also discussed.

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Conference Track: “Nanophotonics”
High Harmonic Generation in (3+1)-dimensional Weyl Semimetals

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Recently, the (3+1)-dimensional Weyl semimetal (WSM), as a new phase of topological quantum matter, has been implemented in a variety of condensed matter systems. The low energy theory of the simplest WSM is described by the Weyl Hamiltonian near the Weyl nodes where the right and the left chirality fermions are separated in the momentum space. Due to the nontrivial topology of the bands, the Berry curvature in the momentum space is nonzero, and we have an appropriate case of the Dirac monopole/anti-monopole realization in the momentum space. As a result, the linear electromagnetic response of the (3+1)-dimensional WSM is described by an axionic field theory with the anomalous electrodynamic effects.

Currently, there is tremendous interest from the strong fields physics perspectives in understanding how the field theory anomalies affect the nonlinear response of WSM. To this end, in the current paper, we investigate the low-energy nonlinear electrodynamics of WSM and analyze polarization-resolved high-order harmonic generation spectra in WSM. Our results show that the spectra in WSM are completely different compared to 2D graphene case. In particular, at the non-collinear arrangement of the electric and Weyl node's momentum separation vectors, anomalous harmonics are generated which are polarised perpendicular to the direction of the pump wave electric field. The intensities of anomalous harmonics strongly depend on the momentum space separation of the Weyl nodes. When the right and the left Weyl fermions are merged, we have a 4-component trivial massless Dirac fermion, and as a consequence, the anomalous harmonics vanish. In contrast to the anomalous harmonics, the intensities of normal harmonics do not depend on the Weyl node's momentum separation vector and resemble the results for a massless 3D Dirac fermion.

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Ultra-Wideband Graphene-based Absorbers for THz Integrated Waveguide Systems

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Historically, terahertz science and technology has been restricted to specialized applications such as radio astronomy due to various technological challenges. Hollow rectangular waveguides are the primary transmission line medium in many terahertz systems due to their mechanical stability, low electromagnetic losses, enclosed nature, and compatibility with active circuit elements. Electromagnetic wave devices such as circulators, couplers and power dividers require that one or more of their ports be terminated to eliminate unwanted signals and ensure correct operation. Waveguide terminations are often realized by short-circuited waveguide sections that present low reflection and absorb the incident energy due to the presence of an absorbing material inside the waveguide [1]. We proposed a new kind of ultra-wideband THz absorber which can be directly integrated into a standard metallic waveguide [2], allowing it to be used in conventional THz systems.

In order to analyze the electromagnetic properties of the absorbing materials in the frequency range from 67 GHz to 500 GHz, the absorbing material has to be embedded inside a waveguide. At the sub-millimeter frequencies, these dimensions get too small to insert any absorber material; therefore, we use vacuum filtration to directly deposit the absorber material inside a specialized waveguide cassette. This cassette can then be integrated with a waveguide system for material characterization. The integration method developed here is easily scalable to different frequency ranges and waveguide geometries and requires only standard laboratory equipment and techniques, making it viable for high-volume production. In addition, by utilising the same method with precision silicon micromachined components [3], our approach could be used to develop compact, low-cost THz waveguide absorbers of complex geometry.

The measured insertion loss between 67 GHz to 110 GHz is greater than 20 dB and exceeds 40 dB at frequencies above 400 GHz. The reflection coefficient of the samples measured below 200 GHz is in excess of −10 dB, indicating that much of the incident energy is reflected by the step change in impedance at the material’s interface at these frequencies. The short electrical length of the samples at these frequencies (0.2λ0 at 88.5 GHz) leads to a relatively low insertion loss, despite the material’s high reflectivity. Above 200 GHz, the GAIN samples exhibit a reflection coefficient below −10 dB.

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REFERENCES

Remote Photocatalysis - Indirect Excitation of Photocatalytic Systems via Plasmonic Modes in Silver Nanowires

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Plasmonic photocatalysis is being a widely explored topic nowadays. The well-established mechanisms of interactions between plasmonic nanostructures and semiconductors, such as hot electron injection, plasmon induced resonance energy transfer or radiative decay of plasmons are described in most studies. Localized surface plasmon resonance (LSPR) modes are mainly considered to be responsible for such interactions. However, another mode exists, which is important for plasmonics and nanophotonics, i.e. surface plasmon polaritons (SPPs) mode. Plasmons in this mode can carry excitation energy for distances far longer than light wavelengths. It can be advantageous also for photocatalysis since such energy can be later transferred to the photocatalytic system. Therefore, such system does not have to be irradiated directly but can be excited "remotely" – only with the energy of SPPs.

In this work we present a new approach to the excitation of photocatalytic systems via plasmonic nanostructures. Using the phenomenon of SPPs propagation in silver nanowires combined with a radiative decay of plasmons, we observed remote excitation (i.e. without a direct irradiation) of photocatalytic systems consisting of TiO2 and a fluorescent probe. The whole process was induced using a focused laser and monitored under fluorescence microscope. Changes in the fluorescent probe emission are the evidence of the photocatalytic process taking place in the system, and therefore, utilization of energy transferred through the nanowire. Observation of such process sheds new light on the mechanisms of plasmonic photocatalysis.

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Analysis of the Fluorescence Intensity Enhancement by Magnetic-Plasmonic Nanoparticles for Biomarkers Detection

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A method for the early diagnosis of diseases based on magnetic nanoparticles with traps for biological markers injected into the blood circulatory system was studied. For effective extraction and non-toxicity of the method, it is recommended to use small magnetic nanoparticles with a diameter of not more than 6 nm [2]. The magnetic force can be used to concentrate extracted nanoparticles for strong signal enhancement [3]. However, magnetic nanoparticles of a few nanometres size are very difficult to manipulate and concentrate by any forces due to the domination of viscosity force [4]. Thus, for the effective concentration of such small nanoparticles using the magnetic system, it is proposed to add larger magnetic nanoparticles (from several tens to several hundreds of nanometres). The fluorescence molecule should be used to detect the signal from biomarkers.

A mathematical model of the fluorescence signal is worked out, and a fluorescent signal is simulated. The model is based on the finite-difference time-domain method. Dependence of the intensity of the fluorescent signal on the distance between fluorescence molecule nanoparticles and the surface of a small magnetic (Fe₃O₄) nanoparticle, and for the surface of a large plasmonic magnetic nanoparticle (covered by small plasmonic layer) is analyzed. It is assumed in the simulation that a plasmon layer is a thin 5–10 nm gold layer. The simulation has shown that magnetite of small magnetic nanoparticles creates a significant attenuation (quenching) of the fluorescent signal when the molecule is at a distance of a few nanometers from its surface, with leads to a significant attenuation of the fluorescent signal (ten and more times). Therefore, in order to get efficient methods, a significant signal enhancement is needed. Simulations have shown that a large enhancement can be achieved by coating large magnetic nanoparticles with a thin metal layer for plasmon enhancement of the field intensity at the dye molecule area. The maximum enhancement of the fluorescent signal is observed at a distance of 5–8 nm of the fluorescent molecule from the surface. A thin dielectric layer of a few nanometers can significantly reduce absorption. An estimation of the intensity of fluorescence signal for the proposed method is performed, and it was shown that significant signal enhancement is possible only in the case of a sufficient concentration of magnetic nanoparticles by a magnetic system. Mathematical modeling of the fluorescence process has shown that the method requires the development of technology to produce two or three-layer magnetic nanoparticles, namely, magnetic nanoparticles having a magnetic core, plasmonic layer, and additional dielectric layer.

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REFERENCES

Merging Polarization Degeneracy and High Localization with All-Dielectric Metasurfaces in Microwave and Near-Infrared Ranges

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The spectrum of electromagnetic plane waves in any isotropic homogeneous medium is twice degenerate with respect to polarization at any frequency and in any direction, because the dispersions of TE- and TM-polarized eigenmodes are absolutely the same. The operational principle of any bulk classical polarizer is based on the removal of the polarization degeneracy by using an anisotropic slab.

Miniaturization and planar technologies lead to the high localization of the electromagnetic signal in the plane of propagation. However, at the same time, the degeneracy is removed. The simplest example is the dielectric slab waveguide demonstrating the propagation of highly localized guided modes with different dispersions of TE and TM modes. So, there is no polarization degree of freedom for planar photonic devices with in-plane electromagnetic wave propagation, since the TE and TM localized modes are not degenerate. It significantly limits the functionality of flat optical and planar photonic devices. In particular, the polarizer of guided waves cannot be implemented without the broadband TE-TM polarization degeneracy.

In this work, we show the possible resolution of this fundamental problem via the nanostructuring of the dielectric slab. We aim merging the polarization degeneracy and high localization for guided waves propagating within an all-dielectric metasurface. Namely, we theoretically study the periodic subwavelength array of cylinders with high refractive index and demonstrate the broadband TE-TM polarization degeneracy of its guided modes. This concept can be transferred to the optical and infrared ranges using other material platforms and opens new opportunities for the polarization control of guided waves such as metasurface-based waveguide polarizer [1]. Another possible implementation includes the self-complementary metasurfaces obeying Babinet’s duality principle [2]. These results could potentially become a platform for new generation of planar photonic polarization devices.

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Depletion Layer Engineering in Core-Shell Metal Oxide Nanocrystals

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The optical and electronic properties of metal oxide nanocrystals (MO NCs) strongly depend on the surface depletion regions, derived from the presence of surface states. MO NCs exhibit a localized surface plasmon resonance (LSPR), offering tunable characteristics enabled by doping, or via electrochemical or photochemical charging. Dynamic control over the LSPR makes MO NCs promising for several optoelectronic and storage applications [1]. By manipulating the NC depletion width, it is possible to control the features of the NCs. The mechanism behind this phenomenon is very complex, and not yet fully understood [2]. In particular, it is possible to engineer the depletion region by varying several parameters, including the material under consideration, the size of the NCs, the presence of multiple core-shell systems, etc. To do this, it is possible to calculate the energy band and carrier density profiles for NCs with different features. In this work, a new framework has been introduced in order to predict the behavior and physics under the MO NCs photodoping process, revealing that the charging mechanism is based on the electronic rearrangement of the energy bands. Numerical simulations were experimentally supported by studying the case of a core-shell structure of ITO/In2O3 NCs, by tuning the thickness of the shell, as well as post-synthetically, both by photodoping and reversible chemical reactions. The engineering of the depletion layer and the consequent manipulation of the electronic structure allows to significantly increase the sensitivity of LSPR and to target specific properties in MO NCs. The fine-tuning of the NCs band structure has enabled an improvement in the charge storage capacity, which represents a step towards fully light-driven energy storage devices [2].

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Multifunctionality of Silver Nanoparticles Embedded in Dielectric Matrices for Optical, Electrical Engineering and Microbiology Applications

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The current tendency in design of compact devices requires integration of different functionalities in the same scheme. A way to respond to this demand is to apply multifunctional components when assembling the device. Typically, these multifunctional components are under the form of piled very thin layers or nanostructures with specific patterns. They offer the possibility for transition from material level of development to system level of applications. For example, to provide a dielectric layer with enlarged and well-controlled electrical properties, one can use metallic nanoparticles dispersed in it.

In this general scheme our scientific approach concerns the multifunctionality of silver nanoparticles (AgNPs) embedded in silica layers to form very thin nanostructures. The attractiveness of AgNPs is based on their multifunctional properties, which allows addressing a large variety of applications, as demonstrated by our team. The optical properties of AgNPs were used to elaborate highly-performant plasmonic structures aiming at a study of the conformational changes of proteins adsorbed on solid surfaces [1]. Fine control of the AgNPs biocide properties was proved essential for fabrication of efficient and environmentally-friendly antimicrobial surfaces [2, 3]. The catalytic properties of AgNPs appear extremely helpful to advance our understanding and describe the role of metals in cosmic dust formation [4]. In particular, this contribution focuses on the electrical charge injection and transport in thin dielectric layers containing AgNPs. The response of these nanostructures under electrical stress was found to be finely controlled via the AgNPs, thus providing solutions to avoid electrostatic issues in MEMS RF switches and HVDC cables [5–7]. The critical for space applications electron emission from dielectrics under irradiation is also shown to be controlled by the incorporated in the dielectric AgNPs [8]. Combination of different AgNPs functionalities offers even larger scope when envisaging device assembly and fabrication.

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REFERENCES

Noncolinear Coupling in Magnetic Multilayers: Modelling and Applications in Spintronics

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Magnetic multilayers play a crucial role in the development of many spintronics applications such as magnetoresistive random access memory (MRAM) and spin-torque nano-oscillators. Possible design parameters for the optimization of device properties include the magnetic material properties of the individual layers as well as their mutual coupling. With regard to the latter, an important effect is the Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling that introduces an exchange coupling between two magnetic layers separated by a nonmagnetic layer, typically made of Ru. Depending on the thickness of the Ru layer this exchange coupling can either be of parallel or antiparallel nature. However, the coupling is always collinear putting serious restrictions on the design of multilayer devices.

Recently, it has been shown experimentally that spacer layers made of RuFe can cause a strong noncollinear coupling of ferromagnetic layers [1]. Furthermore, a precise control over the coupling angle could be achieved by varying the composition ratio of the RuFe layer. This novel effect has a great potential to significantly influence the design of multilayer devices such as spin-torque MRAM. While we developed a micromagnetic model with laterally fluctuating couplings to explain the noncollinear coupling in our original work, this model fails to explain the details of the coupling mechanism especially when it comes to trends in the coupling strength.

In this talk, we will introduce a simple atomistic model for the RuFe spacer layer, which is able to predict the noncollinear coupling depending on layer composition and thickness with an astonishingly high level of accuracy [2]. Furthermore, we will discuss the implications of the novel coupling mechanism on the design of novel spintronics devices.

REFERENCES

Liquid Crystal Templated Chiral Plasmonic and Circularly Polarized Luminescent Films with Dynamic Tunability and Moldability

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Abstract ID #NP-0410

Chiral thin films, exhibiting circular dichroism (CD) or circularly polarized luminescence (CPL), attract considerable interest in the context of fabricating novel types of organic light-emitting diodes, leveraging the bandwidth of data processing and storage, and developing new types of security tags. However, to fully capitalize on their potential, further efforts are required to develop novel strategies enabling enhancement, tuning, and active regulation of chiroptic activity in the solid state.

Our group has developed multicomponent systems exhibiting CD/CPL properties through chirality transfer mechanisms from liquid crystalline (LC) matrix to metal or semiconductor nanoparticles (NPs) [1]. The LC matrix forms helically twisted fibers upon freezing; chirality is then transferred to Au or InP/ZnS NPs that we purposely designed to efficiently mix with the organic material and follow a helical geometry of the twisted filaments. Handedness of the fibers is controlled via chirality synchronization [2] or amplification from minute amounts of a chiral dopant [3], while pitch of the helix can be controlled via organic matrix design [4]. Such films can be dynamically switched and the soft nature of LC matrix enables patterning of the films via a thermal nanoimprinting method. Overall, we developed a useful methodology to achieve tunable and moldable chiral films which may hold significant potential as active, flexible chiroptical materials.

More recently, we proposed that achieving plasmonic NPs having chiral morphology, with hydrophobic coating should enable efficient and large-scale production of integrated chiral organic-inorganic nanocomposites, providing crucial engineering advantages for future generations of soft matter-based functional devices.

ACKNOWLEDGMENTS

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REFERENCES

Micro- and Nanopatterning of Thin Films by Means of Focused Electron Beam

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Due to the increasing demands on electronic and photonic devices, new materials and technologies are researched and developed in order to meet the requirements such as lower dimensions, lower power consumption, new functionalities. Simultaneously, the complexity of electronic and photonic circuits is becoming more and more challenging. Therefore, there is a strong need for flexible high-resolution patterning techniques that enable processing of functional materials. One of the considered methods is direct writing using focused electron beam [1] as, in contrast to conventional photolithography, its resolution is practically not limited by diffraction, patterns can be easily modified on an ongoing basis and there is no need of pattern transfer (e.g. by etching).

The electron beam direct writing can be realized using precursors that are in gaseous or condensed state. Although the gas-phase focused electron beam induced deposition (GP-FEBID) allows for very high resolution and 3D nanoprinting, this is a very slow process and, what is more, introducing of precursors of new materials every time requires modification of gas injection systems of a patterning device. On the other hand, precursors in the condensed phase provide much higher deposition rates, are easily deposited as thin films by spin-coating or dip-coating (like photoresists) and additionally enable easier introduction of new functionalities into materials. For this reason, we develop new materials which can be used as spin-coatable condensed-phase precursors for electron beam patterning.

We show that room-temperature ionic liquids are promising materials for e-beam direct writing because of their unique combination of physicochemical properties such as low vapor pressure, high ionic conductivity, high thermal stability. Moreover, properties of these materials can be easily tuned by modifying cation/anion or mixing them with metal salts [2]. We demonstrate that microstructures containing selected metals can be produced by e-beam patterning of mixtures of ionic liquids and metal salts. Such method of metal patterns formation can be potentially attractive for micro- and nanoelectronics.

Furthermore, we study the possibility of obtaining photonic components by e-beam patterning of sol-gel materials that are based on precursors of SiO2 and TiO2. We show that high-resolution diffraction gratings can be fabricated using sol-gels including titanium alkoxide precursors. Also, we investigate the effect of thermal treatment on the purity of patterned materials as well as the refractive index dispersion of them.

Finally, we demonstrate preliminary results concerning electron beam patterning of ionogels, which are combinations of ionic liquids and oxides formed by sol-gel process. The properties of ionogels make them attractive for flexible wearable electronic devices.

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REFERENCES

Silver Nanowire – Plasmonic Magic Wand

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Abstract ID #NP-0414

The presentation will focus on advocating for uniqueness of silver nanowires, metallic structures with diameters of 100 nm and lengths up to a millimeter [1]. While the diameter of the nanowires is small enough to facilitate localized surface plasmon resonance, their length is sufficiently large to exploit propagation of energy over considerable distances. In combination with advanced nanostructural manipulation, these properties open virtually unlimited playground for interdisciplinary research, which spans over fluorescence enhancement [2–4], remote and high efficiency sensing [5–7], long-range energy propagation [8–10], controlled photocatalysis, heat propagation, etc.

As all of the experiments involve some form of fluorescence microscopy and spectroscopy, surface functionalization, microdroplet deposition, and alike, essentials of the technical aspects will be discussed to the necessary detail.

Experimental demonstrations will include:
1. Plasmonic enhancement of protein fluorescence
2. Real-time single protein detection
3. Remote activation of luminescence
4. Interfacing nanowires with quantum dots
5. Remote photocatalysis

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REFERENCES

Photoluminescence and Nonlinear Optical Properties of Rare-earth doped Borate and Germanate Nanomaterials

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Abstract ID #NP- 0441

It will be presented our recent and interesting results on visible and near infrared emissions (photoluminescence down-conversion and second harmonic generation) of nanomaterials prepared by polymeric precursor and sol-gel methods. The materials studied are based on borate and germanate systems, especially YBO₃, YAl₅(BO₃)₄, BaB₂O₄, Al₂B₂O₇ and Y₂Ge₂O₇ phases, doped with neodymium, ytterbium, europium, thulium and terbium for random lasers, displays, and nanothermometry devices. Some structural, thermal, optical and spectroscopic properties will be presented and discussed.

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REFERENCES


Direct Writing of Atomically Precise Elements for Optical and Sensor Applications

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Abstract ID #NP-0456

Conventional material deposition and lithography techniques can be costly and time consuming, especially for innovation and rapid prototyping. Atomic layer additive manufacturing can alleviate these issues while providing flexibility both in materials and device geometry [1-3]. ATLANT 3D technology provides a platform for Selective Area Direct Atomic Layer Processing (SADALP) in µm-scale areas.

Films deposited with SADALP are closer to bulk than PVD films, and therefore exhibit superior electrical properties suitable for sensor applications. ATLANT 3D technology has been shown to produce high quality, crystalline, atomically precise thin films [3]. It has been used to fabricate temperature and capacitive sensors with sensitivities that meet or exceed those of devices made using conventional PVD techniques [4].

ATLANT 3D platform provides flexibility in deposition geometry that enables a range of optical applications that require high precision fabrication techniques. Optically transparent films can be used as atomically thin protective layers for device encapsulation, as well as for atomic corrections of existing lenses that have some defects. Alternating deposition materials enables multilayer mirror fabrication of custom dimensions. Smooth thickness gradients can be used to manufacture ultrathin optical lenses. Overlapping depositions with discrete steps enable manufacturing of binary lenses and phase masks. Growth rate enhancement in rastered printing mode using ATLANT 3D technology can produce periodic grating structures. [5] Conformal coatings on complex surfaces can act as functionalization layers or seed layers for further material deposition through e.g. electrochemical processes.

REFERENCES

TRACK 6

“TRANSPORT PROPERTIES IN NANOSCALE SYSTEMS”
Fatty Alcohol Nanoemulsions as Latent Functional Thermal Fluids for Energy Management

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Phase change material nanoemulsions (PCMEs) are gaining increasing attention as promising two-phase thermal fluids for advanced energy management in several applications such as solar harvesting or the cooling of electronic components \cite{1, 2}. PCMEs are prepared by dispersing fine droplets of a phase change material into a conventional carrier fluid with the aid of appropriate surface-active agents \cite{3}. Hence, these novel thermal media combine the additional latent heat absorbed/released during the melting/crystallization of the dispersed phase with the better transport properties of the thermal fluid used as continuous phase.

This work presents an experimental study on the preparation and characterization of thermal and physical properties of fatty alcohol nanoemulsions based on an ethylene glycol:water mixture (20\%:80\% in mass). Concentrations from 2 to 8\% in mass of cetyl alcohol (with a melting transition at 48 °C) were dispersed by means of a solvent-assisted emulsification method \cite{2} using a mixture of anionic and non-ionic surfactants. The size of dispersed droplets was monitored through time and after samples were subject to several cooling-heating cycles to rule out possible destabilization issues. Phase change transitions were characterized in terms of temperature and latent heat, and subcooling reduced to a few degrees when either hydrophobic silica nanoparticles or eicosyl alcohol (melting point at 64 °C) were used as nucleating agent. Even if emulsions showed thermal conductivities larger than that of the bulk cetyl alcohol, this transport property reduced with increasing concentration of dispersed phase. Finally, samples exhibited desirable Newtonian viscosities or slight shear thinning behavior.

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REFERENCES


The Impact of the Anchoring Group on Thermal Stability and Electrical Conductivity of Self-Assembled Monolayers

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Abstract ID #TPNS-0112

Self-assembled monolayers (SAMs) on metal substrates are one of the most widely used types of organic nanostructures in different aspects of nanotechnological applications [1]. The potential use of SAMs strongly depends, however, on the stability of their chemical bonding to the substrate and the thermal stability of formed monolayers. Another key factor that has to be considered for applications in molecular/organic electronics is their conductance. Here, we present an in-depth characterization of purely aromatic SAMs on gold and silver substrates in terms of structure, stability, and electrical conductivity. The vast spectrum of different possible anchoring groups, including commonly used thiolates, selenolates, and carboxylic acids together with recently proposed N-heterocyclic carbenes (NHCs) [2], was investigated using a multidisciplinary approach. The stability of bonding and thermal stability was probed using secondary ion mass spectrometry (SIMS) measurements. The conductivity was examined using large-area molecular junctions based on eutectic gallium-indium alloy (EGaIn).

It was demonstrated that the thermal stability is strongly influenced by the anchoring group and is maximized using thiols [3] and NHCs [4] for silver and gold substrates, respectively. The conductivity of thiols, selenols, and carboxylic acids is, on the contrary, independent of the chosen bonding group [3-5] and is approximately one order of magnitude higher than analogous oligophenyl-based SAMs (considered as highly conductive). This rather unexpected independence is rationalized by a tentative model considering redistribution of charge density along the molecular framework. The superior conductivity could be of use in electrodes functionalization of OFETs (organic field effect transistors) for providing improved charge transport at the metal-organic interface. Surprisingly, NHC SAMs of very similar structure to that of the aforementioned group, have strongly insulating properties [4] with electrical conductivity nearly 4 orders of magnitude lower than that of standard alkanethiols of comparable length (which are already considered as insulators). This result is directly connected to the imidazolium moiety that serves as an anchoring group in NHCs and provides a SAM-based platform of paramount importance for the electronic industry, as it is desirable to have both thin and insulating films for gate electrode functionalization. As the film thickness of NHCs is ~3 times smaller than that of alkanethiols of similar conductivity, it translates to ~3 times higher capacitance of the junction, the key parameter responsible for source-drain current in OFET devices.

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REFERENCES


Numerical Modeling of Oil Flow Through Porous Polymer Membranes

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Numerical modeling is a powerful tool for optimizing the application of the membranes with various geometry, i.e., pore shapes, fibers' diameter, their arrangement or morphology production. The models can have a wide range of applications in drug delivery systems aiming for a controlled release via the porous membrane.

In our work, we electrospun poly (vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB) to thin fibers. Changing the molecular weight of the polymer, we obtained both nano- and micro-PVB fibers. Those membranes were imaged with a focused ion beam scanning electron microscope (FIB-SEM, FIB Zeiss Neon 40EsB CrossBeam, Carl Zeiss NTS GmbH, Germany) to get 2D cross-section images. These images were stacked together to obtain 3D models of nano-PVB and micro-PVB membranes. Then, these models were used in the numerical simulation performed in COMSOL Multiphysics (v. 5.6, COMSOL Inc., Sweden). All the membranes' voids were filled with oil. The simulation conditions were: temperature of 23 °C, slip wall conditions for all fibers (fixed walls), and no-slip for the domains' outer walls. The oil inlets through the upper wall (ZX plane) with static capillary pressure. The capillary pressure \( p \) was calculated from the Young-Laplace equation: \( p = 2 \gamma \cos(\theta)/r \), where \( \gamma \) is surface tension for evening primrose oil (32.5 mN·m\(^{-1}\)), \( \theta \) is oil wetting angle on the PVB membranes (5 °), and \( r \) is the radius of pores. The average value for nano-PVB fibers is 0.83 µm, for micro-PVB fibers: 2.67 µm. The capillary pressure for nanofibers equals 22.25 Pa and for microfibers: 6.91 Pa. The oil, considered as incompressible material, outflows on the bottom through the ZX plane with static zero pressure.

The nano- and micro-PVB membranes are characterized by different dimensions of fibers and pores. Nano-PVB fibers are 0.3 ± 0.08 µm thick, with 0-3 µm of pore size, while micro-PVB fibers are 1.0 ± 92 µm thick with 0-9 µm of pore size [1]. These geometrical features substantially affect the fluid flow through those membranes [2]. The microfiber-based membranes need 4 times longer for oil to pass through in comparison to nanofiber-based membranes [3]. The numerical simulation of the oil flow through the membranes showed a higher velocity profile for nano-PVB membranes. The higher capillary pressure presented in the nanofibrous membrane causes the higher flow velocity of oil than in the microfibrous one. Hence, the capillary pressure driven by the pore size is a crucial parameter for the oil flow velocity. The porous membranes' geometry allows for selection of desired speed of delivering the oil. The controlled oil flow through the porous polymer membranes has many applications in dermatological patches for skin treatments.

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REFERENCES

Bilinear Magnetoresistance in 2D Electron Gas with Cubic Rashba Spin-Orbit Interaction

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Abstract ID #TPNS-0118

Bilinear magnetoresistance (BMR), the component of magnetoresistance that scales linearly with both magnetic and electric fields, is a phenomenon emerging in materials with strong spin-orbit coupling [1, 2] as a second-order response to the external electric field. Linear dependences on both fields provide opportunities for reading or writing binary data in new spintronic devices.

In recent years, a high-mobility two-dimensional electron gas formed at the interfaces of perovskite-oxides, e.g., LaAlO3/SrTiO3 (LAO/STO), exhibiting strong spin-orbit coupling, became an interesting platform for the investigation of the spin-orbit driven phenomena [3, 4]. It was experimentally shown that such systems reveal a k-cubed form of Rashba spin-orbit interaction [4]. What is more, the cubic form of Rashba SOI can also describe the two-dimensional (2D) hole gas in III-V semiconductors [5].

Using Green’s function formalism and diagrammatic approach, we study BMR in a 2D system described by the model Hamiltonian that includes an isotropic k-cubed form of the Rashba spin-orbit interaction. Such a Hamiltonian captures the spin and electronic properties of two-dimensional gas at the surfaces or interfaces of transition metal oxides or in p-doped semiconductor heterostructures [6].

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Bilinear Magnetoresistance in Graphene

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Abstract ID #TPNS-0120

Spin-orbit interaction in systems subject to external electric field can lead to the current-induced spin polarization of charge carriers (CISP), which, in turn, results in a new kind of magnetoresistance effect [1]. This new effect scales linearly with both electric and magnetic fields, and therefore it is called the bilinear magnetoresistance (BMR). Within the low-energy Hamiltonian of graphene with strong Rashba spin-orbit interaction and in an external in-plane magnetic field, we derived CISP and BMR in terms of the Green’s function formalism. We present detailed characteristics of these two effects and show similarities and differences to BMR obtained in other 2D systems such as topological insulators [1], [2] and 2D Rashba gas [3]. Our model may be simply extended to other graphene-like materials.

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Stable Negative Capacitance in MOSFET Transistors: Possible or Not?

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Abstract ID #TPNS- 0143

In recent years, there have been intense attempts to create devices that would use a negative capacity effect predicted by Rolf Landauer as early as 1976 [1]. If successful, such attempts would lead to a real breakthrough in the scaling of modern electronics devices [2, 3]. In particular, the use of ferroelectrics for this purpose, which show stable ferroelectric properties at film thicknesses of 5 nm and less; are CMOS-compatible and thermally stable in combination with silicon; allow deposition on 3D substrates; have a wider band gap than silicon and form a significant contact barrier for the electrons from the silicon conduction band. The principal possibility of reduction (in case of success) the subthreshold swing and supply voltage to the values below the fundamental limits define the great interest in the creation of these systems using ferroelectrics.

We consider a silicon MOSFET, in which the gate insulator is formed from thin layers of a dielectric SiO2 and a weak ferroelectric HfO2. We study the possibility of implementing a stable negative capacitance of the insulator in such a system, which would open the principal possibility to reduce the subthreshold swing to the values below the threshold, 60 mV/decade at room temperature, and supply voltage to the values below the fundamental Boltzmann limit, 0.5 V, which would be an important step towards further miniaturization of MOSFETs. It is shown theoretically that it is possible to achieve a transient negative capacitance of a ferroelectric in the situation when the charge at the capacitor plates increases more slowly than the ferroelectric polarization. Note that the negative capacity is fundamentally transient. Its temporal stabilization in thin dielectric and ferroelectric layers requires stable positive free energy and capacity of the whole system. Therefore, the effect of the negative capacitance of a ferroelectric itself cannot be manifested "outside" the ferroelectric, including the transistor applications.

This negative result has its own value for the development of corresponding applications in perspective directions. Actually, the failure of the above attempts is obviously a simple explanation. Indeed, even the negative capacitance of the ferroelectric can be stabilized, the total capacitance of the gate insulator always remains positive. And since the capacitance is not a local, but a global characteristic of the system, it is this total capacitance (rather than the negative capacitance of the individual ferroelectric layer) included in all equations that describe the operation of the transistor, and in the expression for the subthreshold swing. Therefore, it is unrealistic to hope that the negative capacitance effect will help reduce the subthreshold swing below the critical value, and thus contribute to further miniaturization of the MOSFET.

REFERENCES

Quantum Effects in Low-Temperature Thermal Expansion of C$_{60}$ Fullerite Doped with $^4$He Impurity

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Abstract ID #TPNS-0155

Since Kroto et al. discovered C$_{60}$ by laser vaporizing graphite into a helium stream in 1985 [1], fullerenes are at the heart of nanotechnology and have attracted significant attention from the scientific community. In this work, we clarify the influence and possible competition of contributions to the thermal expansion of fullerite doped with helium impurities, quantum effects of various natures with the help of a detailed study of the thermal expansion of C$_{60}$ fullerite doped with $^4$He impurity.

The method of precision low-temperature dilatometry in the temperature range 2-24 K was used to study the thermal expansion of C$_{60}$ fullerite doped with $^4$He impurity at a temperature of about 2 K. The nature and obtained values of thermal expansion strongly depended on the concentration of $^4$He impurity in fullerite. In the temperature range 2-5 K, the thermal expansion of the $^4$Hex-C$_{60}$ system is negative, that explained by the tunneling movement of $^4$He atoms in the system of cavities in the fullerite crystal lattice. The contribution of this process to thermal expansion decreases with an increase in the C$_{60}$ impurity concentration and a decrease in the probability of tunneling of helium atoms between the cavities of the crystal lattice. In the temperature range 4.5-22 K, the thermal expansion of the $^4$Hex-C$_{60}$ system is dominated by the transformation between different modifications of the fullerite orientational glass. The tunneling nature of this transformation determines the negative contribution of this process to thermal expansion, as well as the hysteresis and thermal expansion anomalies that was observed in this temperature range. The intensity of these processes associated with the tunneling phase transformation between the orientational fullerite glasses increases with an increase in the helium impurity concentration in the fullerite.

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Magnetoresistance of Graphite Nanoplatelets Simultaneously Modified with Nickel and Iron

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Abstract ID # TPNS-0184

The work presents the results of magnetoresistance investigations of graphite nanoplatelets (GNPs) modified with both iron and nickel. The graphite nanoplatelets have been obtained by sonication of source thermoexfoliated graphite (TEG) in acetone medium. The modification of GNPs has been carried out with method of reducing the metal from the water-salt solution in the stream of the mixture of gaseous helium and hydrogen. As results the graphite nanoplatelets with 60 % mass concentration of metal (Ni 80 wt% : Fe 20 wt%) on the surface have been obtained. The structural and morphological state of modified GNPs as well as the character of metal particles distribution in nanocarbon structures are described in detail in [1]. The investigations of magnetoresistance for bulk specimens of source TEG and for GNPs modified only with nickel and only with iron have been carried out. Studies have shown that the character of the temperature and field dependences of the magnetoresistance, as well as the angular dependences of the magnetoresistance for bulk specimens of source TEG, GNPs modified with only one metal and GNPs modified by two metals are significantly different. For source TEG magnetoresistance is described by classical equation. Magnetoresistance is square with respect to the magnetic field, increases with decreasing temperature. That is due to the increase in mobility with decrease of temperature. For modified with Nickel GNPs the dependence Δρ/ρ(B) does not contain any features (hysteresis, change in the sign of the magnetoresistance when changing the mutual orientation of the magnetic field and current through the specimen), associated with the presence of magnetic metal on the surface of GNPs. For modified with both iron and nickel GNPs, the dependence Δρ/ρ(B) contains a pronounced hysteresis. The change in the sign of the magnetoresistance at different mutual orientations of the magnetic field and the current through the specimen is also observed. These features in the dependence Δρ/ρ(B) indicate that for simultaneously nickel and iron modified GNPs, the interaction between charge carriers in GNPs and the magnetic moments of ferromagnetic metal atoms takes place. Previously, this effect was observed exclusively for modified with magnetic metals CNTs.

REFERENCES

Investigation of Thermal Transport Properties of Multilayer Porous Silicon Based Hybrid Nanostructures by Photoacoustic Technique

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Abstract ID #TPNS-0242

In this work we report the results of an experimental study of photoacoustic transformation in nanostructured hybrid systems “multi-layered porous silicon (mlPSi) / liquid”. The mlPSi nanostructures were grown by programmable electrochemical etching of highly doped monocrystalline silicon. The informative photoacoustic response was formed by the photoacoustic cell with gas-microphone registration in a classical configuration. The approach based on modelling the temperature distribution inside the nanostructure allows us to evaluate the thermal conductivity of mlPSi before and after incorporating the liquid inside the porous network. As a result of our experimental investigations, the rise of the thermal conductivity (up to 1.6 times) of the hybrid system “mlPSi / liquid” compared to the initial system was found. The presented approach can be easily adapted to study other composite nanostructures with a solid-liquid interface. The results obtained for hybrid systems “mlPSi / liquid” provide new paths for its practical implementation in the field of sensors and thermal management devices.

ACKNOWLEDGMENTS

This paper contains the results obtained in the frames of the project “Hotline” ANR-19-CE09-0003 and “DropSurf” ANR-20-CE05-0030. V. S. and V. K. gratefully acknowledge the financial support from the National Research Foundation of Ukraine for supporting this work by Grant NO. 2020.02/0067.
Polarization-Dependent THz Response in HgCdTe Hot-Electron Bolometer Detectors

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Abstract ID #TPNS-0247

The paper reports the detection of polarization-dependent photocurrent in HgCdTe hot-electron bolometers with the receiving antennas which manifest by the linear and circular photogalvanic effect under the radiation of elliptically polarized THz laser. The detectors under the study are based on the bulk epitaxial grown Hg1-xCdxTe (x=0.2) film with the normal band order structure (Eg > 0) in the crystallographic plane (013). The spin-splitting manifested in our experiment by the circular photogalvanic effect. The non-magnetic semiconductor alloy HgCdTe with a strong spin-orbit coupling belongs to the non-centrosymmetric non-gyrotropic point symmetry group Td. That is why the appearance of spin-splitting phenomena is possible due to the structure-induced asymmetry connected with a uniaxial strain of the film which leads to lowering film symmetry and the occurrence of gyrotropy in the crystal. The studied detectors show the spin-polarization dependent sensitivity related to absorption by free carriers on the laser generation frequencies of 1.07 THz and 0.6 THz range at T = 80 and 300 K. Thus we have shown the possibility of implementation of the polarization-sensitive photogalvanic spintronic detector on the basis of the bulk HgCdTe hot-electron bolometers of micron size with the focusing planar antennas operating even at ambient temperature without applying any external magnetic field.

ACKNOWLEDGMENTS

This work was partly supported by the Volkswagen Foundation Partnerships-Cooperation Project “Terahertz optoelectronics in novel low-dimensional narrow-gap semiconductor nanostructures” (project number 97738,) and the NAS of Ukraine, project No. ІІІ-3-22.
Thermal Conductivity Evaluation of the Carbon-Based Nanofluids with Photoacoustic Approach

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Abstract ID #TPNS-0250

The report will be devoted to the investigation of thermal transport properties of several types of carbon-based nanomaterials, namely graphene oxide and carbon nanodots fabricated with two different approaches. As the basic liquids, we investigated water, horological oil, and polyethene glycol. Specifically, the latter liquid belongs to the phase change materials, and it is promising for application for thermal energy storage. We observed a nonlinear rise in the thermal conductivity of nanofluids with increasing the volume fraction. Such a nonlinear rise in thermal conductivity could be explained by the influence of the interfacial nanolayer between the particles. This was taken into account for the effective thermal conductivity model. Specifically, the effects of nanolayer thickness, nanoparticles size, volume fraction, and thermal conductivities of basic fluid, nanoparticles, and nanolayer were considered.

ACKNOWLEDGMENTS

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Thermal Transport Properties of Nanoporous Silicon with Molecular Dynamics Approach

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Abstract ID #TPNS-0261

Understanding thermal transport at the nanoscale is the significant issue for improvement of the stability and reliability of various devices due to their overheating and hotspots arising. In this context, the information about heat transfer perturbations due to the interfaces and edges of the nanomaterials is essential for the thermal management of the mentioned above devices. As one of the main mechanism responsible for the perturbation is phonon scattering processes due to presence of elastic stresses [1], elastic properties mismatching [2] and the modifications of the parameters [3] at the interfaces. In order to illuminate the light on the mechanisms impact on thermal transport properties, we investigated thermal transport properties of nanoporous silicon with atomistic simulations and analytical modelling. Specifically, equilibrium molecular dynamics approach was chosen for the examination of thermal conductivity of the system. We considered the situation when the porous matrix is represented by the periodic system with the spherical pore. Different radii of the pore and the system periods were studied to find the most significant factor influenced the thermal conductivity reduction in the studied nanostructured material. Moreover, the analytical model which describes the temperature behaviour of thermal conductivity was proposed based on the kinetic theory of phonons. As the input components for the modelling, we used phonons’ density of states, dispersive curves, lifetime calculated with molecular dynamics.

Thus, we obtained the dependence of the thermal conductivity of porous silicon as a function of porous diameter and material’s porosity for temperatures in range from 300 K to 1100 K. The latter allows us to reformulate the kinetic scattering theory for phonons to takes into account the presence of the scattering events at the pore’ edge. Moreover, as the results of our work, we found that under room temperature the specific surface area is the crucial factor of thermal conductivity reduction of nanoporous silicon. With increasing of the temperature, the impact of the specific surface area is vanished, and thermal conductivity of the system is mainly defined by the phonon-phonon scattering.

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This paper contains the results obtained in the frames of the project “Hotline” ANR-19-CE09-0003 and “DropSurf” ANR-20-CE05-0030. V. S. gratefully acknowledge the financial support from the National Research Foundation of Ukraine for supporting this work by Grant NO. 2020.02/0067.

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Nitrogen Donor in Silicon: Towards Room Temperature Operation of Single Electron Tunneling Devices

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Abstract ID # TPNS-0346

Following the proposal by Kane where the nuclear spin of Phosphorous (P) donor in silicon (Si) serves as a qubit, extensive work has been done on a few donor(s) based device where single electron tunneling effect are observed only at low temperature [1-2] due to shallow nature of donors (mostly As and P) [1-2]. Some results on high temperature operation of such devices due to quantum confinement, dielectric confinement, and donor’s cluster formation has also been reported, but these operations highly depend upon state of art techniques [3-4].

One of the approach to overcome the problem of low temperature operation of single electron tunneling devices is to use the donor atoms having deep energy levels within the band gap. Some of single donors (Nitrogen (N), Carbon (C) etc.) and double donors (Tellurium (Te), Selenium (Se), Sulfur (S)) [5] have one order higher binding energy than shallow donors. A few theoretical proposals have been reported for quantum architecture using double donors [5]. However, no major investigation was performed on deep single donor for such purpose. We mainly focused on such a deep donor i.e., N in silicon, which has binding energy 190 meV lying below the conduction band as high as four times of thermal fluctuations.

In this report, the atomistic structure of a silicon nanowire surrounded by gate all around and tunnel coupled with source and drain reservoirs has been substitutionally doped by single P and N donors. The silicon nanowire transistor is constructed by Quantum ATK software along 100 directions with wire diameter 15 Å and length 54.3 Å. The n+ type source and drain leads are doped with concentration of 1x10²¹ cm⁻³ within a length of 10.8 Å. In order to understand the properties of the systems under study, mainly PDOS and LDOS spectra are simulated based on density functional theory. For further probing these properties, electrical characteristics are also simulated using a semiempirical extended-Hückel method, mainly at T = 300 K and 5 K. We observed that N-doped silicon nanowire could have very high binding energy compare to P-doped silicon nanowire. We also observed N-doped silicon nano-transistor shows strong single-electron-current (SET) peak at room temperature, while a broader SET peak observed in case P-doped transistor having same device configuration.

Thus, the present study will provide a direction for the fabrication of single atom devices at room temperature.

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REFERENCES

Modeling Charge Transport Through Nanomaterials

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Abstract ID #TPNS-0448

Interfaces have long been studied for their fundamental importance in material microstructure as well as their broad applicability in electronic devices. However, the challenge involved in characterizing the relation between structure and electron transport of a large number of interface combinations inhibits the search for interfaces with improved functionality. Therefore, we develop a novel high-throughput screening approach that combines computational and theoretical techniques. We use a Density Functional Theory + U (DFT+U) quantum mechanical formalism to produce effective Schrödinger equations, which are solved by wave packet propagation to simulate charge transport across the metal/oxide interface. We demonstrate this method on nanomaterials, including molybdenum disulfide with vacancies interfacing with metals and dielectric materials.

This research is relevant for the activities in COST Action CA18234 titled “Computational Materials Sciences for efficient water splitting with nanocrystals from earther abundant elements”. This COST Action intends to focus on bridging the knowledge gaps between different theoretical methods and computer codes in order to facilitate the discovery of novel materials for energy conversion. The objectives of this challenge include building an organized network of European scientists working on achieving greater scientific understanding of water splitting and developing approaches for reliable and realistic multi-scale modelling of nano-oxides material architectures. I will display the networking activities and opportunities that are available by joining our COST Action.

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[8] https://www.cost.eu/actions/CA18234/
Electron Transport in Discontinuous Metal Thin Films

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The electronic conduction mechanism in discontinuous thin films of discrete metal nanoparticle islands on insulating substrates was the subject of intense study in the 1960s and 1970s when the Neugebauer and Webb model [1] of interisland charge transfer between a sparse distribution of charged islands of radius r separated by gaps s became generally accepted [2]. The key features of the model were that the charged island density is governed by Maxwell-Boltzmann statistics with an electrostatic nanoparticle charging energy:

\[ \delta E = \frac{q^2}{2C} \]  

where \( q \) is the electronic charge, \( \varepsilon \) is the effective dielectric constant and \( C \) is the island capacitance, and that electron transfer between islands takes place by electron tunnelling, giving rise to an Arrhenius relationship between the conductance \( \sigma \) and absolute temperature \( T \):

\[ \sigma = \sigma_0 \exp\frac{-\delta E}{kT} \]  

The model’s acceptance relied primarily on the experimental agreement with theory [2] for:

- The general form of (1), except for inconsistency in the values of \( \varepsilon \) determined experimentally from the equation,
- The observation of a square root dependence of \( \delta E \) on the electric field, (like a Schottky effect,) as predicted theoretically, and
- The variation of the strain coefficient of resistance with the island separation as predicted for tunnelling.

Despite the general acceptance of the model, which was later supported by subsequent work on the coulomb block and single electron transistor, there was recognition that several experimental observations in the literature remained unexplained [2]. These discrepancies included:

- Theoretical conductance orders of magnitude too low in comparison with experiment
- Capacitance \( C \) orders of magnitude too high when determined from Bode plots of the frequency dependent impedance (\( C >> \frac{q^2}{2\delta E} \))
- Anomalous effects with asymmetrical island sizes at the contacts, including:
  - Diode effect (i.e., a polarity dependent resistance)
  - A \( (R1||C1 + Rs + R2||C2) \) equivalent ac impedance model from Bode and Cole-Cole plots
  - Pseudo-inductance (apparent resonance) with extreme asymmetries
- Switching effects
- The absence of any significant “back bias effect” which should dominate the Boltzmann distribution of charged islands, and
  - That film resistance does not scale with length

The last point always seemed to indicate that the contacts play an unrecognized role, but no consistent pattern was identified.

A modified model based on contact injection has been developed [3, 4], (also incorporating charge separation and recombination,) and computer simulations have explained all the discrepancies above at a qualitative level [5].

- The diode effect is the result of the difference between electron and hole injection, which produces a greater field at the positive contact, exacerbated by asymmetrical island structures at the contacts.

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Capacitance values determined from the frequency dependence of film impedance are consistent with the parallel capacitance between the contacts and the adjacent islands.

The injected charge is much greater than the calculated thermally activated Boltzmann distribution, which explains why (a) the experimental conductance is much greater than previous calculations, and (b) back bias is ineffectual in modulating film conductance.

The initial charged island density is given by the Boltzmann distribution, but then the film conductance grows with time and the injected charge, which causes the pseudo-inductive effects.

Quantitative experimental verification of the revised theory awaits films of stable, known, reproducible structures. The paper concludes with a survey of possible techniques to achieve satisfactory samples, e.g., polymer coated colloids.

**REFERENCES**


TRACK 7

“NANOMAGNETISM & MAGNETIC MATERIALS”
Merging of Spin-wave Modes in an Obliquely Magnetized Thin Magnetic Nanodisk

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Abstract ID #NMM- 0020

Among the most important dynamic characteristics of magnetic micro- and nano-elements are the spectrum and structure of spin-wave (SW) eigenmodes. The majority of works were concentrated on highly symmetric systems [1, 2]. On the other hand, the breaking of geometric and/or magnetic state symmetry can result in new qualitative features which were not observed in a symmetric case.

Here we study the evolution of spin-wave resonance (SWR) spectra of thin circular magnetic dots in a saturated state when the external magnetic field makes some angle with the disk normal. Although, as it is known from previous studies [3], for a small deviation of the field from the dot normal SW modes split, an unexpected regularization of the resonance spectra takes place at a certain angle, and only one prominent peak is observed at this angle. At larger angles, SWR spectra again consist of several resonance peaks.

Using micromagnetic simulations and analytical theory, it has been shown that the observed behavior is due to the degeneracy of several spin-wave modes when the transition of spin-wave dispersion from forward wave type to backward one takes place. The phenomenon of SW modes merging is observed for a wide range of nanodot diameters and can be useful for magnetic noise spectrum narrowing. For 40 nm thick Permalloy dots, this phenomenon cannot be observed for dots with a diameter below 500 nm due to too large intermode distance in k-space, making it impossible to fall within a flat dispersion region at any field deviation angle.

REFERENCES

Imaging Magnetic Domain Structure of a High Entropy Alloy: Effect of Applied Magnetic Field

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High-Entropy Alloys (HEAs) are recently introduced materials consisting of numerous—at least five—elements in nearly equal-atomic concentrations [1]. Studying them, previously unexplored phase fields in multidimensional phase diagrams are now being explored. The HEA concept is based on a thermodynamic balance between mixing entropy and enthalpy, which defines values of several critical parameters that determine the formation of simple or complicated phases. As such, micro- and nano-structural control will inevitably define the properties development with respect to targeted future application fields [2]. Physical properties, like magnetism, are of great interest for these materials, even though they are not, so far, extensively analyzed [3]. Particularly, the exploration of the magnetic domain structure and its correlation with the micro- and nano-structural features of the materials is of high scientific value [4].

In this work, we study the influence of the magnetic history on the alteration of the magnetic domain patterns in polycrystalline FeCoNiAl\(_{0.9}\)Mn\(_{0.9}\) High Entropy Alloy (HEA). For the study, we introduce a combinatorial method of Electron Backscatter Diffraction and Magnetic Force Microscopy imaging, which reveals specific magnetic domain structures in the grains of different crystallographic orientations. It is found that in the HEA polycrystal, an increase of the applied magnetic field affects the formation of magnetic domains and leads to a transition from a labyrinth-like pattern to a dotted domain configuration, which is expressed differently in the differently oriented grains.

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Spin Waves in Bilayers of Vanadium Dichalcogenides

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Abstract ID #NMM- 0066

Two-dimensional Van der Waals materials are currently of great interest. This is due to unique magnetic and electronic properties of these materials. We have analyzed theoretically and numerically the spectrum of spin waves (magnons) in two-dimensional bilayer systems of VX\textsubscript{2} (X=S, Se, Te) transition-metal dichalcogenides (TMDs) \cite{1}. The vanadium atoms within individual atomic layers are coupled ferromagnetically, while the exchange coupling between V atoms located in different planes is either ferromagnetic or antiferromagnetic, depending on the stacking type of individual layers in the VX\textsubscript{2} bilayer system. The magnon spectra are considered in the case of T-type and H-type bilayers. We have analyzed in detail these spectra as a function of magnetic anisotropy and external magnetic field applied perpendicularly to the layers.

The spin-wave dispersion relations have been derived analytically within the spin-wave theory of antiferromagnets, in terms of the Holstein-Primakoff transformation combined with the Bogolubov diagonalization scheme. For numerical discussion, the intra- and interlayer exchange parameters, as well as the magneto-crystalline anisotropy, have been evaluated within the method based on the density functional theory (DFT). The corresponding magnon spectra have been also simulated numerically. From the DFT calculations we have also determined the Curie temperatures of the VS\textsubscript{2}, VSe\textsubscript{2} and VTe\textsubscript{2} bilayer systems, which are close to or well above the room temperature, in agreement with the corresponding literature.

In the case of antiferromagnetic TMD bilayers, the system undergoes a field-induced transition to the spin-flop phase, which evolves into the saturated ferromagnetic phase for sufficiently strong magnetic fields. Our considerations also show that an extreme case of direct field-induced metamagnetic transition between antiferromagnetic and saturated ferromagnetic phases may occur as well. Existence of different phases depends on the material parameters, especially on the interlayer exchange and anisotropy constants. We have analyzed the spin wave spectra in all these phases and showed how these spectra change at the phase transitions and how they evolve with increasing magnetic field. We have taken into account both, in-plane and out-of-plane magnetic anisotropy.

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\textbf{REFERENCES}

Stochastic Generation Regime of an Antiferromagnetic Spin Hall Oscillator

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Abstract ID #NMM-0073

Antiferromagnetic (AFM) spin Hall oscillator (SHO) is a novel spintronic device capable of operating on THz frequencies, while under the action of electrical DC current [1]. These devices have been theoretically studied regarding possible mutual synchronization of such systems, using them for neuromorphic computing, and external synchronization under the action of the external harmonic signal [2-3]. The next step is an investigation of the stochastic generation regime in SHO when the system generates stochastic oscillations and not determined harmonic output. Here we show that such a regime indeed exists in the investigated system and can be tuned by the appropriate selection of external signal frequency and amplitude. Stochastic generation manifests itself as spike-like impulse generation with random time intervals between them. The average time interval between impulses is about 10ps. This is an order of magnitude faster than existing random generation systems. Obtained results can be useful for the creation of ultra-fast spintronic devices for probabilistic calculations. Furthermore, such THz frequency stochastic elements are the first of their kind and open up a lot of possibilities for future applications both in the field of spintronics and electronics.

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Morphological, Structural, and Magnetic Properties of Perovskite-type Solid Solutions

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Abstract ID #NMM-0077

Multiferroics are multifunctional materials, which display two or more ferroic orders simultaneously. The possible control of magnetism via electric field or vice versa leads to potential application in different areas, including solar cells, random access memories, microwave phase shifters, etc [1]. Bismuth ferrite (BiFeO₃), rare earth (RMO₃ M = Fe, Mn) ferrites or manganites possesses both ferroelectric as well as (anti)ferromagnetic properties, which makes them ideal candidates for further investigation and plausible commercialization [2].

In this work three perovskite-type: YₓGd₁₋ₓMn₀.₉₇Fe₀.₀₃O₃ [3], Y₁₋ₓGdₓFeO₃ [4], and Bi₁₋ₓGdₓFe₀.₈₅Mn₀.₁₅O₃ solid solutions series were investigated. All compounds were prepared by sol-gel technique, in which solid materials can be obtained through gelation by progressive polycondensation reactions rather than precipitation or crystallization. With the use of ethylene glycol as complexing agent, this method allows stoichiometry control and high degree of homogeneity for the final products. Numerous characterization techniques, like X-ray diffraction, Raman, FT-IR and Mössbauer spectroscopies, were employed to investigate the relationship between the chemical composition and the structure. Furthermore, scanning electron microscopy analysis were performed for surface morphology investigation. Lastly, room temperature magnetization measurements were done for all solid solutions.

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Influence of Temperature on the Noise-Handling Properties of a Sub-Terahertz Detector Based on an Antiferromagnetic Tunnel Junction

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Abstract ID #NMM-0078

In this paper we numerically analyze the performance of a subterahertz frequency signal detector based on an antiferromagnetic tunnel junction (ATJ) in the presence of thermal noise. The detector is a four-layer ATJ Pt/Ir$_{0.2}$Mn$_{0.8}$/MgO/Pt employing the tunneling anisotropic magnetoresistance effect, which is connected to an external circuit of 50Ω impedance. Using the detector model developed in [1] and assuming that MgO tunneling barrier thickness and ATJ resistance-area product are the temperature-dependent values, we calculate the temperature dependences (T = 4.2–300 K) of the detector output DC voltage $U_{DC}(T)$ and its signal-to-noise ratio $SNR(T)$ in the presence of low-frequency Johnson-Nyquist noise. Our results indicate although the dependence $U_{DC}(T)$ is rather weak (temperature-dependent changes of $U_{DC}$ are less than ±5%) the $SNR(T)$ substantially increases with a decrease of temperature $T$ and for an ATJ with optimal parameters [1] at cryogenic temperatures ~10 K it can reach ~ 500. The obtained results can be useful for the development and optimization of spintronic detectors based on antiferromagnetic nanostructures.

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Subterahertz Frequency Signal Source Based on an Antiferromagnetic Tunnel Junction Embedded in a High-Q Dielectric Resonator

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Abstract ID #NMM-0096

It has been shown recently [1] that the embedding of a spintronic nanostructure based on a canted antiferromagnet (AFM) in a high-Q dielectric resonator can be useful for the creation of (sub-)terahertz-frequency (TF) signal sources providing output AC power of ~ 1 µW. In this paper, we consider an alternate design of such a sub-TF signal source, where an antiferromagnetic tunnel junction (ATJ) is used instead of a spin Hall oscillator based on a canted AFM [1].

The ATJ is considered as a layered Pt/AFM/MgO/Pt structure consisting of a bottom current-driven platinum (Pt) layer adjacent to a layer of an Ir$_{0.2}$Mn$_{0.8}$ antiferromagnet separated by a MgO spacer from the top Pt layer. A DC electric current flowing in the bottom Pt layer excites the transverse spin current flowing into an AFM layer due to the spin Hall effect and, therefore, the rotation of magnetic sublattices of Ir$_{0.2}$Mn$_{0.8}$ with (sub-)terahertz frequencies. Consequently, this rotation creates radiation of the same frequency, while the oscillations’ energy is collected due to the resonant properties of the high-Q dielectric resonator used in the device (in our model the resonator is rectangular).

Using a simple electrical model of an ATJ developed in [2], we investigate the power generation in the considered system. We consider an ATJ as a simple circuit consisting of oscillating resistance, capacitance, and inductance. Such a circuit is connected to an external circuit (high-Q dielectric resonator) with some impedance, thus, generated AC power is transferred from an ATJ to an external circuit with an account of the impedance mismatch effect. Note, that the impedance of the resonator depends on the frequency and type of the excited resonance oscillations (TMmnp or TEmnp) as well as the position of ATJ inside the resonator.

In this paper we derive a general expression for the output AC power $P_{ac}$ of the source based on an ATJ placed inside a high-Q dielectric resonator. We found that it substantially depends on the position of an ATJ inside the resonator and the type of the excited oscillation mode (TMmnp or TEmnp). The optimization of the above-mentioned parameters reveals that the generated power of such a source could exceed 1–10 µW in the frequency range of 0.1–1 THz for the majority of low-frequency sub-TF TMmnp or TEmnp oscillation modes (for example, the indicated power was calculated for the TM111 mode). The obtained results can be useful for the development and optimization of (sub-)terahertz frequency signal sources based on AFM spintronic nanostructures.

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Control of the Bose-Einstein Condensation of Magnons in Nanosized YIG Films by the Spin Hall Effect

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The recently discovered rapid cooling mechanism allows for the formation of magnon Bose-Einstein condensates (BECs) solely driven by short electric DC heating pulses in micro-sized spintronic structures based on nano-thick yttrium iron garnet (YIG, Y₃Fe₅O₁₂) films [1]. At the same time, the possibility of a purely spin-current-induced magnon BEC formation originating from the spin-Seebeck effect (SSE) [2] and the spin-Hall effect (SHE) [3] is of considerable research interest, allowing for DC-polarity-dependent condensation and manipulation of the magnon condensate’s lifetime. In the case of a BEC caused solely by the rapid cooling mechanism [1], the subsequent condensation process is driven by excess thermal magnons arising from a rapid decrease in phonon temperature. A temperature drops fast enough for BEC formation is achieved during the cooling of micro-sized YIG/Pt structures heated by short DC pulses. Here, I report on the control of the formation of the rapid cooling-induced magnon BEC using the SHE [4]. Using a sufficiently thin YIG film (34 nm) and a 7 nm-thin sputtered Pt layer as a heater and spin injector, a significant SHE-driven magnon injection or annihilation was provided during the 100 ns-long electric DC-pulse application. The magnetization dynamics was measured by means of Brillouin light scattering (BLS) spectroscopy. The key experimental finding is that the SHE-driven change in the magnon population during the pulse action modifies the threshold of the BEC formation process developing after the pulse is turned off. In particular, we achieved significant enhancement or complete suppression of magnon condensation in the near-threshold regime for additional magnon injection or annihilation, respectively. A threshold voltage shift of −8% or +6% is observed for the injection or annihilation cases, respectively.

Moreover, it was found that the application of a longer (1.0 μs) DC electric current pulse triggers the formation of a nonlinear localized magnonic bullet below the linear magnon spectrum. After the pulse termination, the magnon BEC, as before, is formed at the bottom of the linear spectrum, but the nonlinear bullet continues to exist, stabilized for an additional 30 ns by the same process of the rapid cooling-induced magnon condensation [5].

Thus, combining typical spintronic effects with quantum magnonics, we demonstrate control of the magnon BEC formation via the polarity of the applied electric current pulse and the ability for a stimulated condensation of excess magnons to all highly populated magnonic states.

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Origin of Exchange Bias in Nanocrystalline CoCr$_2$O$_4$

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A detailed magnetic study focusing on exchange bias (EB) effect is reported in this article for CoCr$_2$O$_4$, of different particle sizes and interparticle separation. Three nanocrystalline samples with particle sizes 30, 12 and 7 nm have been prepared using conventional sol-gel technique. The third sample is embedded in amorphous silica host to study the effect of interparticle separation. All the nanoparticles are characterized using powder X-ray diffraction (PXRD) pattern and Transmission Electron Microscope (TEM) images. Analysis confirms the absence of any impurity phases in the samples. Studies of thermal variation of magnetization reveal, a clear transition from collinear ferrimagnetic (FiM) to non-collinear spiral (TS), and finally to a lock-in transition (TL) for all the samples. These nanoparticles demonstrate conventional EB effect (loop shift followed by increase in coercivity when cooled under a static magnetic field). Despite core-shell like structure, EB appears at low temperature and monotonically decreases with increase in temperature. EB field vanishes soon after crossing the spin spiral ordering temperature (TS) regardless of different size and interparticle interaction. CoCr$_2$O$_4$ with particle sizes 30 and 12 nm reveal EB originating from surface effect and interaction of rotatable and frozen spins with FiM core. Surface effect is controlled in CoCr$_2$O$_4$ with particle size 7 nm as embedded in SiO$_2$. Analogous EB effect is noted for this sample too with beautiful exhibition of memory effect in different temperature (T) and time (t) dependent protocols originating from superspin glass like ground state. A bulk sample of same composition with particle size > 150 nm reproduces similar result, which rules out the origin of EB in this material because of surface effect. These results indicate that, the origin of EB in this well-known multiferroic material is because of an inherent magnetic inhomogeneity developed because of interaction between long range collinear ferrimagnetic spins and short range non-collinear spiral spins below spiral ordering temperature [1-5]. A basic understanding regarding the origin of EB mechanism and memory effect in a suitable state in potential multiferroic CoCr$_2$O$_4$ is certainly interesting from the point of view of multifunctional functionalized materials useful to explore application-oriented device fabrication.

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Control of Structural and Magnetic Properties of Epitaxial Co$_2$FeGe Films by Deposition and Annealing Temperatures


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Full-Heusler alloys are of great interest due to unique physical properties and potential applications in different areas of science and technology. They can demonstrate half-metallic ferromagnetic properties which are crucial for spintronics and magnonics applications. Recently a lot of investigations were focused on Co$_2$FeGe which is half-metallic ferromagnet with relatively high magnetization and high Curie temperature. It has been shown [1] that the structural, magnetic and magnetodynamical properties of polycrystalline films of Co$_2$FeGe can be efficiently controlled by adjustment of the technological conditions of film preparation. Here we extended the study on epitaxial films deposited on MgO (001) single crystalline substrates.

Co$_2$FeGe films of 60 nm and 120 nm thickness were deposited by magnetron co-sputtering (Orion- 5 AJA Int. deposition system) on single crystalline MgO (001) substrates. The substrates were held at room temperature (RT) and at elevated temperatures of 300 °C and 500 °C. Also, the influence of the annealing for the samples deposited at RT was investigated. X-ray studies (Rigaku SmartLab diffractometer) confirmed epitaxial growth [110]CFG // [100]MgO. For the annealed samples and the samples deposited at elevated temperatures additional superstructural peaks 111 and 113 were observed which are characteristic of atomically ordered phase L2$_1$. The films prepared at RT are tensile stressed in the film plane. Magnetic resonance measurements were carried out in plane and out of plane at room temperature by the electron spin resonance spectrometer Bruker ELEXSYS E500 operating at 9.87 GHz (X-band) equipped with the automatic goniometer and a coplanar waveguide broadband (2-20 GHz) vector network analyser was used for the measurements with the magnetic field applied in the film plane. Magnetic characterization of the films were performed using a Quantum Design MPMS 5S SQUID magnetometer.

The main difference from polycrystalline films studied earlier [1] is that the elevated temperature deposition does not improve the magnetic characteristics of the films. Samples deposited at elevated temperatures show just a small increase in the saturation magnetization and the effective magnetization values due to the atomic ordering of the alloy and the decrease of tensile stresses. But simultaneously it results in decrease of forth order magnetocrystalline anisotropy value as well as the increase of coercivity and damping parameter. The annealing also improve the atomic ordering of the alloy. But for annealed films a dramatic decrease of the damping parameter and the increase of saturation magnetization were observed. Thus, the properties of the films could be effectively tuned in a wide range. This paves the way for different technological applications.

REFERENCES

Homogenization and Chemical Ordering in Co-Pt Thin Films

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Binary alloys based on CoPt are attractive as a materials for spintronics, permanent magnets applications and data storage devices due to the high and tunable coercivity combined as well as an excellent corrosion resistance [1].

The formation of chemically ordered CoPt magnetic phases is intensively studied both in thin films and in nanoparticles [2, 3]. In Co-Pt alloys, a large coercive field and magnetic anisotropy can be achieved even in chemically disordered alloys due to short-range order [4]. We have implemented a systematic structural and magnetometry study of the diffusion-controlled formation of a homogeneous CoPt alloy by vacuum heat treatment of Pt/Co stacks, where diffusion processes are driven by diffusion-induced grain boundary migration mechanism.

Layered stacks of Pt(14 nm)/Co(13 nm)/Ta(3 nm) were magnetron sputter deposited and annealed in vacuum of 10⁻⁶ mbar in the temperature range of 200 °C – 550 °C. The structure, chemical composition and magnetic properties of the films were analyzed by X-ray diffraction, secondary ion mass spectrometry, scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy, and VSM magnetometry.

We demonstrate that a Co-Pt alloy with a homogeneous structure is formed after annealing at temperature above 500 °C. Despite the fact that long-range chemical order in CoPt film was not formed, thermal treatment leads to an increase of the coercive field. We attribute the short-range chemical ordering as a mechanism responsible for the formation of a local anisotropy in Co-Pt alloy. In this respect, our study suggests that the diffusion mechanism relying on grain boundary migration can be used to promote short-range ordering in binary magnetic alloys.

These results will motivate further studies of diffusion processes and the formation of hard magnetic chemical

REFERENCES

Nonreciprocal Acoustic Waves in Hybrid Magnetoelastic Microstructures

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Nonreciprocity of wave propagation is a fascinating physical phenomenon, highly desirable and already widely used in microwave signal processing technique. Being dependent on the simultaneous breaking of time- and space-reversal symmetry, wave nonreciprocity is prohibited in the majority of simple physical systems. Current state-of-art nonreciprocal devices rely on the nonreciprocity of electromagnetic waves in ferrite-based waveguides, which are almost impossible to miniaturize below several centimeters size.

A viable alternative for lightweight and compact applications are microwave solid-state acoustic devices, which are famous by their nice characteristics in the frequency band from 100 MHz to several gigahertz. However, symmetry of fundamental laws of mechanics prohibits nonreciprocity of pure acoustic linear waves in solids (inherent nonreciprocity can be realized in moving or rotating media, e.g., gases or liquids, which are not applicable above sound/ultrasonic band). Therefore, a source of acoustic waves nonreciprocity was searched in the interaction of elastic subsystem with other subsystems of a media or structure.

One of the most promising way of inducing of acoustic waves nonreciprocity is the utilization of magnetoelastic coupling with spin waves. In this talk, we present various approaches for the magnetoelastic induction of acoustic wave nonreciprocity, starting from historically first approach [1], and covering the most recent theoretical ideas [2-3] for giant and wide-band nonreciprocity in hybrid magnetoelastic microstructures, as well as their experimental realizations [4-5]. Current progress in the field allowed to realize nonreciprocity of surface acoustic wave propagation losses with unprecedentedly high isolation up to 48 dB. In addition, an approach for the realization of SAW phase nonreciprocity and its first experimental observation in LiNbO3/FeGaB/Al2O3/FeGaB heterostructure are reported. Challenges and directions of further improvement are also discussed.

REFERENCES

Size and Heat Treatment Effects in Magnetoresistive Properties of (Ni$_{80}$Fe$_{20}$)$_{70}$Au$_{30}$ Nanostructured Thin-film Materials

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The magnetoresistive properties of thin films can be influenced by varying thickness [1]. Thus it has become an issue of considerable importance, primarily if thin ferromagnetic films are used for data storage devices. The size effect can be significant in magnetoresistance (MR) when the thickness of the samples is comparable to the average size of a single-domain granule [1, 2].

Consequently, we prepared the series of (Ni$_{80}$Fe$_{20}$)$_{70}$Au$_{30}$ thin-film samples by the electron-beam co-evaporation technique within the range of thickness from 10 to 45 nm to investigate the role of the size effect in their magnetoresistive properties. The concentration of the non-magnetic atoms was chosen at 30 at.% since, according to Ref. [2], for systems based on permalloy and noble metal at close concentration, the maximum MR value was observed. Moreover, the heat treatment effect on magnetoresistive properties of investigated systems was discussed. For this purpose, the samples were annealed isothermally at 400, 500, 600, and 700 K for 20 min. The longitudinal and transverse MRI measurements with current-in-plane geometries were held in a magnetic field with induction to $B = 0.5$ T. The equation has calculated the value of magnetoresistance $MR = (R(B) - R(B_0))/R(B_0)$, where $R(B)$ is the current value of resistance in the magnetic field $B$; $R(B_0)$ is the resistance of the sample in the field of the $B_0$.

According to our studies of as-deposited samples, the field dependences of magnetoresistance have an anisotropic character. For all samples, the MR of thin films in both geometries decreases with increasing induction of the applied external magnetic field, while the field dependences of the longitudinal and transverse MR coincide within the measurement error. Also, a feature of these dependencies is the lack of hysteresis and saturation in magnetic fields up to 500 mT. This is due to small single-domain ferromagnetic nanoparticles that form in the condensation process and require large fields for remagnetization. The value of the magnetoresistive effect was found to depend on the thin film thickness and takes a maximum of about 0.43 % at room temperature at the maximum thickness of investigated samples $d = 45$ nm. The variation of field dependences of magnetoresistance after annealing has shown that the annealing to 400 and 500 K does not lead to a change in MR value for all investigated samples. The nature of the MR effect remains isotropic. The transition to anisotropic nature of magnetoresistance was observed at 600 K. This behavior is also associated with changes in the crystal structure of the samples. In the process of heat treatment, there is a growth of ferromagnetic grains; they touch each other, and there is a process of coalescence, which leads to the formation of multidomain nanoparticles. As a result, the magnetic configuration of the system changes, which leads to a weakening of the magnetoresistive effect.

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Chiral Effects in Curvilinear 1D Antiferromagnets

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Spin-orbit phenomena enable new ways to manipulate magnetic ordering in low dimensional magnetism. In this respect, materials with antiferromagnetic (AFM) coupling attract significant attention providing higher eigenfrequencies, a rich diversity of material properties and perspectives of spatial scaling due to the absence of significant stray fields. Tailoring the geometry of AFM thin films and nanowires in planar or 3D architectures provides a possibility for changing magnetic responses by means of shape of the magnet [1, 2]. In this presentation, we will discuss the recently discovered chiral and anisotropic effects peculiar for curvilinear 1D antiferromagnetic spin chains. A spin chain arranged along a space curve is a prototypical example of a curvilinear AFM whose shape is characterized by the curvature and torsion. In the absence of intrinsic anisotropy, the dipolar interaction renders the tangential direction as the hard axis of the anisotropy [3]. The competition of this geometry-tracking interaction with the nearest-neighbor exchange leads to the emergence of additional anisotropic and chiral energy terms, whose coefficients are determined by the curvature and torsion. The geometry-induced anisotropy is of easy-axis type and determines the direction of the AFM order parameter within the easy-plane enabled by the dipolar interaction. The geometry-induced inhomogeneous Dzyaloshinskii-Moriya interaction (DMI) renders the curvilinear spin chain acting as a chiral helimagnet. The latter leads to the geometrically-driven helimagnetic phase transition in helix-shaped AFM spin chains [3].

A local variation of the anisotropy axis can result in the non-collinearity of the neighboring spins in curvilinear spin chains. 1D AFMs exhibit the parity-breaking effect, which forbids exchanging sublattices once they are selected. This leads to the emergent magnetization at non-collinear AFM textures Therefore, in any spin chain arranged along a space curve, there is a weak ferromagnetism proportional to the curvature and torsion of the curve [4].

Spin chains arrangements on a planar surface have the only ground state along the binormal direction [3]. In presence of an external magnetic field, their spin-flop state is dependent on geometrical parameters. The spin-reorientation transition is followed by the canted state for small enough rings due to the exchange-driven DMI. Furthermore, we will show that the curvature-induced DMI results in the hybridization of spin wave modes and enables a geometrical-driven local minimum of the low frequency branch, which opens exciting perspectives to study long-lived collective magnon states in AFMs [3]. This positions curvilinear 1D antiferromagnets as a novel platform for the realization of geometrically tunable chiral antiferromagnets for antiferromagnetic spinorbitronics and fundamental discoveries in the formation of coherent magnon condensates in the momentum space.

REFERENCES

Curvature-induced Local & Nonlocal Chiral Effects in Curvilinear Ferromagnetic Shells and Wires

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Conventional magnetic nanoscale devices are based on planar thin films and straight racetracks hosting magnetic topological solitons. Recent progress in fabrication and characterization methods allows to realise and study of complex-shaped planar and three-dimensional (3D) architectures. In the planar case, boundaries of nanodots lead to the formation of inhomogeneous textures, such as vortices and antivortices. In 3D, the magnetostatic interaction favours a spatially inhomogeneous shape anisotropy, which acts as easy-axis anisotropy along wires or hard axis of anisotropy perpendicular to the film surface. These interactions track the sample geometry and enable curvature-induced symmetry-breaking effects, such as topology-induced magnetization patterning and emergent anisotropic and chiral responses of the Dzyaloshinskii-Moriya interaction (DMI) type [1, 2].

Curvature-induced magnetic responses can be classified as being local or nonlocal. In ferromagnets, local effects stem from the exchange interaction and DMI. The curvature-induced DMI originates from exchange: it is linear in curvatures and has the symmetry of the interfacial DMI. Its strength can be comparable with typical values of the intrinsic DMI. This is experimentally confirmed by the stabilization of chiral domain walls (CDW) on the apex of a Permalloy parabola-shaped stripe [3]. The strength of the CDW depinning field gives an estimation for the curvature-induced DMI constant and can be tuned by the geometry. In contrast to curvature itself, also curvature gradients offer a possibility to pin CDW, which was studied with an example of a circular indentation with a conic cross-section profile. This geometry supports circular CDWs described by the forced skyrmion equation, where the effective force acts as the stabilizing factor for large-radius skyrmion and skyrmionium states [4]. The magnetostatic interaction is a source of novel curvature-induced chiral effects, which are essentially nonlocal, in contrast to the conventional DMI [5]. The effect emerges in shells with non-zero mean curvature due to the non-equivalence between the top and bottom surfaces of a geometrically curved shell. It is possible to show that the analysis of nonlocal effects in curvilinear shells can be more intuitive with a split of a conventional volume magnetostatic charge into two terms: (i) tangential charge, governed by the tangent to the sample's surface, and (ii) geometrical charge, given by the normal component of magnetization and the mean curvature. In addition to the shape anisotropy (local effect), four additional nonlocal terms appear, determined by the surface curvature. Three of them are zero for any magnetic texture in shells with the geometry of minimal surfaces. The fourth term becomes zero only for the special symmetries of magnetic textures.

The impact of local and nonlocal chiral effects on magnetic textures in curvilinear architectures will be discussed in this presentation.

REFERENCES

Dzyaloshinskii-Moriya Interaction and Domain Wall Damping in Ultrathin Nanostripes

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Abstract ID #NMM-0207

Asymmetric ultrathin magnetic thin films represent intriguing material platforms, which support emerging fundamentals effects, such as skyrmion and topological [1] Hall effects and fast motion of chiral magnetic non-collinear textures [2], that underlie prospective memory and logic devices based on spin-orbit torques. Such asymmetric stacks can provide strong perpendicular magnetic anisotropy and Dzyaloshinskii-Moriya interactions (DMI), which is necessary for the stabilization of chiral non-collinear magnetic textures. As the performance of spin-orbiteronic devices is determined by the static and dynamic micromagnetic parameters [3], it is crucial to determine all internal micromagnetic parameters for the particular layer combination and sample geometry. In particular, the speed of a domain wall (DW) based racetrack is determined by the DMI constant, D, and the DW damping parameter, α. The necessity of having strong DMI requires the utilization of ultrathin magnetic (~1 nm) layers, which implies polycrystalinity and compromised structural quality, that substantially enhances the magnetic damping compared to bulk. Accessing this parameters typically requires dynamic experiments, whose interpretations are cumbersome due to the creep regime.

Here, we present the experimental and theoretical investigation of tilted DWs in perpendicularly magnetized asymmetric //CrOx/Co/Pt layer stacks with the surface-induced DMI. We will discuss two possible theoretical mechanism for the appearance of titled DWs: (I) A unidirectional tilt could appear in equilibrium as a result of the competition between the DMI and additional in-plane easy-axis anisotropy, which breaks the symmetry of the magnetic texture and introduce tilts [4]. (II) A static DW tilt could appear due to the spatial variation of magnetic parameters, which introduce pinning centers for DWs [5]. A moving DW can be trapped in a tilted state after the external driving field is off. Based on these theoretical approaches, we perform a statistical analysis of the DW tilt angles obtained in statics after the external magnetic field used for the sample demagnetization was off. We found that the second approach confirms the experimental observations and allows to determine self-consistently the range of DW damping parameters and DMI constants for the particular layer stack. Using two reference fields, which provide two characteristic tilt angles, allow us to retrieve the range of DMI strength D≥0.8 mJ/m² and DW damping parameters α≥0.1. The upper limit for the DMI constant agrees with an independent transport-based measurement giving D=0.9±0.13 mJ/m², which further refines our estimate of the damping parameter α=0.13±0.02. Thus, the combination of the proposed method with standard metrological techniques opens up opportunities for the quantification of both static and dynamic micromagnetic parameters based on static measurements of the DW morphology.

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Spin-wave Resonance in Arrays of Nanoscale Synthetic Antiferromagnets

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Abstract ID #NMM- 0211

In recent years, much attention has been paid to the development of new magnetic metamaterials for their further use in modern spintronic and magnonic applications [1]. Various approaches, from multilayering of nanostructures to patterning of array-arranged nanoelements, enable additional functionalities, increasing the feasibility of manufactured devices [2]. Operating on significantly smaller scales, when linear sizes are of the order of characteristic exchange length, such systems exhibit non-trivial magnetization dynamics. The increased role of exchange coupling alters the internal structure of standing spin waves and their inherent number of modes [3]. This also applies to synthetic-antiferromagnet (SAF) or ferrimagnet nanoelements, which provide unique control over their ground magnetic state [4].

As we have recently shown [5], three-layer SAF nanostructures may introduce an additional higher-order resonance, caused by the asymmetry and dipole interactions between the layers. Here, we highlight other SAF-specific features in the array of small-sized elliptic nanodisks, subject of our current study. By means of FMR spectroscopy, we are able to experimentally observe the single-mode spin dynamics and its anisotropic behavior in the array plane. Our micromagnetic simulations show that this mode retains almost uniform excitation within each ferromagnetic layer, being non-typical for structures of a larger size. We also demonstrate strong resonance field shift of about 700 Oe when the magnetization is rotated from the major to minor axis. Relying on the performed analytical calculations, we show that this shift cannot appear exclusively due to the shape anisotropy of an individual SAF element.

We describe the single resonance, unique to 75-nm nanodisks, as a hybridized mode, which combines both the main and edge-type oscillations. This is the result of the small size of SAF elements approaching the characteristic exchange length. In addition, we believe that the strong uniaxial anisotropy, although originates from the elliptical shape of the elements, is significantly enhanced by the hybrid character of the single mode. Its spatial distribution strongly depends on magnetization direction, which effectively increases the energy required to excite the mode along minor axis. The results show how the geometry parameters affect spin-wave dynamics in small SAF systems, providing new perspectives in the development of high-end magnetic devices.

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Flexible Magnetoreceptive Switch for On-Skin Touchless Human-Machine Interaction

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Artificial magnetoception, i.e., electronically expanding human perception to detect magnetic fields, is a new and yet unexplored route for interacting with our surroundings. This technology relies on thin, soft, and flexible magnetic field sensors, dubbed magnetosensitive electronic skins (e-skins) [1]. These devices enable reliable and obstacle insensitive proximity, orientation and motion tracking features [2, 3] as well as bimodal touchless-tactile interaction [4].

Although, basic interactive functionality has been demonstrated, the current on-skin magnetoreceptors are not yet employed as advanced spintronics-enabled switches and logic elements for skin compliant electronics. The major limitation remains primarily due to the use of in-plane magnetized layer stacks, sensitive mainly to the magnetic fields oriented within the sensor plane. This prevailing in-plane sensitivity has prevented them from becoming intuitive switches or logic elements for interactive flexible electronics, as the natural actuation axis of switches is out-of-plane. Flexible Hall effect sensors [5, 6] could provide out-of-plane sensitivity, but not intrinsic logic functionality.

In this work, we present the very first tunable magnetoreceptive platform for on-skin touchless interactive electronics based on flexible spin valve switch elements with dedicated out-of-plane sensitivity to magnetic fields [5]. The device is realized on a flexible polyethylene naphthalate (PEN) foil relying on Co/Pd multilayers with perpendicular magnetic anisotropy and synthetic antiferromagnet as a reference layer. Owing to the intrinsic tunability, these interactive elements can provide fundamental logic functionality represented by momentary and permanent (latching) switches and reliably discriminate the useful signals from the magnetic noise. The flexible device retain its performance upon bending down to 3.5 mm bending radii and withstand more than 600 bending cycles.

We showcase the performance of our device as on-skin touchless human-machine interfaces, which allows interactivity with a virtual environment, based on external magnetic fields. Depending on the material properties of the on-skin switch used, the virtual functions can be impervious to (latching) or controlled by (momentary) ambient magnetic stimuli. We envision that this technology platform will pave the way towards magnetoreceptive human-machine interfaces or virtual- and augmented reality applications, which are intuitive to use, energy efficient, and insensitive to external magnetic disturbances.

ACKNOWLEDGMENTS

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REFERENCES


Magnetic and Chemical Structure at Co/α-Fe$_2$O$_3$(0001) Bilayers

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Abstract ID #NMM- 0239

Current spintronics is strongly oriented towards systems where a ferromagnet is in close proximity of an antiferromagnet (AFM). Spintronic devices based on AFMs offer unique properties, such as robustness against magnetic field perturbations, fast spin dynamics and lack of stray fields. Most of AFMs are oxides, which means that details of the chemical, electronic and magnetic structure at the metal-oxide interfaces are crucial for understanding the physics and technology of spintronic devices. Co films on hematite α-Fe$_2$O$_3$(0001) have been subjected to comprehensive experimental studies in the past as a prototypical exchange coupled metal-oxide system [1, 2]. Here we present comparative studies of Co-hematite systems using methods with chemical and magnetic sensitivity: conversion electron Mössbauer spectroscopy (CEMS), X-ray photoemission electron microscopy (X-PEEM), X-ray Absorption Spectroscopy (XAS) and magnetooptic Kerr effect (MOKE).

The hematite α-Fe$_2$O$_3$(0001) layers (typical thickness 10 nm), were prepared in a multi-chamber ultra high vacuum (UHV) system by oxidation of the pre-deposited magnetite Fe$_3$O$_4$(111) films, grown on MgO(111) substrates with Pt(111) buffer layers using oxygen-assisted molecular beam epitaxy (MBE). The film growth and oxidation processes (annealing for 5 hours at 500 °C and oxygen partial pressure of 1x10$^{-5}$ mbar) were controlled in situ under UHV by CEMS to ensure perfect hematite stoichiometry. Low-temperature CEMS measurements revealed the absence of the Morin transition in the hematite films down to 100 K. The wedged cobalt films (thickness range 0.2-3 nm) were grown by MBE at room temperature. A reference area without Co was included. All films were covered with a thin MgO layer for ex situ measurements.

Angle dependent CEMS measurements showed that the zero-magnetic field distribution of the Néel vectors in hematite is different in the uncoated and Co-coated α-Fe$_2$O$_3$(0001) areas of the heterostructure. In the latter case, a uniaxial anisotropy is induced perpendicular to the magnetic field applied for previous Kerr measurements, whereas the bare film shows the 3-fold symmetry of the magnetic anisotropy.

The X-PEEM and XAS experiments were performed at the SOLARIS National Synchrotron Radiation Centre [3]. Images series were taken along the wedge as a function of the Co thickness for the X-ray energy covering the L2,3 edges for iron and cobalt for left and right circular polarization of the X-ray beam. In that way XMCD-images and spatially resolved XAS and XMCD spectra could be extracted for sample regions of interest. The exact match of the ferromagnetic domain structure at the Fe edge (the domain structure is due to reduced hematite at the interface) and Co edges was shown. Moreover, a strong XMLD signal for Co/α-Fe$_2$O$_3$/Pt/MgO(111) with the uniaxial anisotropy at both the Fe and Co edges appeared (the Co-XMLD signal originates from the interfacial Co monolayer oxidized to CoO, as clearly seen from XAS).

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REFERENCES

Strong Influence of Magnetic Order on the Low-Temperature Specific Heat of Heusler Alloys

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The metamagnetic Ni-Mn-X (X = In, Sn, Sb) Heusler alloys exhibit unique properties, such as shape memory effect, magnetocaloric effect, and giant magnetoresistance effect. These properties are connected with the magnetostructural martensitic transformation from ferromagnetic parent austenitic phase to martensitic phase with weak magnetism. The noticeable changes in the magnetic properties are observed in these alloys depending on the concentration of X. In particular, the martensitic transformation occurs mainly in the lower concentration range of X.

It was considered previously that the low-temperature specific heat of magnetic solid consists of two parts: electronic term and phonon contribution, which is described by the Debye equation. The magnetic (spin-wave) contribution to the specific heat was considered negligibly small. However, the experimental studies showed that the specific heat value measured for Ni50Mn50-xInx alloys with x<15, being in antiferromagnetic or paramagnetic martensitic phase, is significantly different from that measured for the alloys with x>16, being in the ferromagnetic (FM) parent state [1]. Due to this, the theoretical approach to the determination of the magnetic part of the specific heat of ferromagnetic solid was proposed and applied to the number of non-stoichiometric Ni50Mn50-Inx alloys [2]. It was shown that the disregard of magnetic contribution to the specific heat of FM solid results in the noticeable underestimation of Debye temperature and overestimation of the specific heat of electron subsystem of FM solid.

The elaborated theoretical approach [2] was applied to the number of Ni-Mn-Sn and Ni-Mn-Sn-Co Heusler alloys for the elucidation of the spin-wave contribution to the low-temperature specific heat of alloys. Both theory and experiment confirm that the spin-wave contribution to the low-temperature specific heat of ferromagnetic solid critically depends on the Curie temperature. The evaluation of spin-wave contribution to the specific heat of different Heusler alloys allows to compute the real dependence of Debye temperature on the concentration of X and to account for the contribution of an electron subsystem. The separation of different contributions to specific heat elucidates the role of magnetic ordering on the properties of metamagnetic shape memory alloys, such as Ni-Mn-In, Ni-Mn-Sn, Ni-Mn-Sb.

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REFERENCES

Skyrmion Nucleation on a Surface of Topological Insulators

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Abstract ID #NMM-0243

Skyrmion nucleation induced by spin-transfer torques at an interface of a topological insulator and a ferromagnetic insulator is investigated. Due to strong spin-orbit coupling on a surface of topological insulators, which enhances the effect of spin torques, efficient manipulation of skyrmions is expected and therefore, topological insulators could provide the ideal platform to achieve high-performance skyrmionic devices. Using micromagnetic simulations and energetics, we evaluate properties of the skyrmion nucleation on a surface of topological insulators, such as nucleation time, critical electric field, and skyrmion numbers. We show that the nucleation time is inversely proportional to the applied electric field. We also identify the Gilbert damping and temperature dependences of the critical field. Furthermore, we analytically evaluate the effect of the Dzyaloshinskii-Moriya interaction and demonstrate that the temperature dependence can be explained by the reduction of a magnon excitation gap due to the self-energy corrections.
Beyond CMOS Computing with Ferroelectric Rashba Semiconductors

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Abstract ID #NMM-0248

Information and communication technology is going to use 20% of the world’s total electricity by 2030. That unsustainable trend requires architectures far beyond the well-established CMOS platform. A remarkable pathway was suggested in 2018 by Intel in the work titled “Beyond CMOS computing with spin and polarization” [1], in which they have shown that the combination of spin currents and multiferroics is a master choice for attojoule-class logic gates.

In this context, Ferroelectric Rashba semiconductors (FERSC) [2] have gained a growing attention. FERSC are characterized by a one-to-one relation between the direction of the ferroelectric polarization and the spin helicity in their Rashba-type spin texture. As so, they are promising platform for the non-volatile control of generation and detection of spins in semiconductors towards spin-based, ultralow power electronics. Most of the experimental work concentrated on germanium telluride (GeTe) [3], a robust ferroelectric at room temperature, for which the ferroelectric control of the spin chirality in Rashba bands was experimentally unveiled [4].

This talk we will first review the main findings about FERSC, including the demonstration that the ferroelectric polarization of epitaxial thin films of GeTe can be reliably switched back and forth by electrical gating and used to effectively reverse a sizeable spin-to-charge conversion by spin Hall effect [5]. GeTe thus allows for logic-in-memory devices, where the information is conveniently stored in the ferroelectric state and the read-out is provided by spin-to-charge conversion. Then, we will show our progresses in the realization and investigation of beyond CMOS devices, exploiting a combination of conventional e-beam lithography with the innovative thermal scanning probe lithography.

This research will show how ferroelectric Rashba semiconductors can provide a path towards non-volatile spin-based computing beyond CMOS.

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REFERENCES

Controlled Recovery of Biomolecules from Model and Complex Biotechnological Systems using Magnetic Nanoparticles

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Abstract ID #NMM-0265

Magnetic nanoparticles (MNP) have the ability to adsorb different types of molecules, including proteins, lipids and polysaccharides. Therefore, they are a useful bioseparation tool; however, selective adsorption of a target molecule or group of molecules onto MNPs is still a challenge. Efforts have been made to obtain this specificity by performing surface functionalization, common in chromatography resins. Nonetheless, functionalization increases the price, rendering nanoparticles less suitable for certain large scale applications. Our final goal is to trigger selectivity for specific biological components in complex environments using inexpensive bare inorganic nanomaterials. In this work, we offer a broad picture of adsorption of biomolecules onto MNPs [1] starting with a defined model system and then [2] moving onto very complex systems such as biotechnological broths, in which the microorganism dictates the biomolecule composition, and the environment is defined by the cultivation needs.

Firstly, we quantify the whole content adsorbed through individual analytical methods and perform surface characterization and secondly, we identify particular molecules that show selective interaction by SDS-PAGE and mass spectrometry, in order to understand if their intrinsic characteristics, such as their pl, hydrophobicity or size, drive the adsorption. The model mixture comprises BSA, sodium oleate and dextran as model molecules representing proteins, lipids and carbohydrates, respectively. We have determined that pH plays a key role for adsorption: in the case of proteins, mainly due to electrostatic interactions; for the fatty acids due to the formation of structures; and in the case of the sugars, such as dextran, no influence of pH was observed. We used microalgal and bacterial lysates, i.e. Microchloropsis salina and E. coli as very complex systems and the results reveal that proteins, lipids and carbohydrates spontaneously bind onto the MNP surface. We obtained selectivity by using additives such as cysteine, changing the partition of solute molecules between the liquid and the surface of the solid phase. We present hints regarding the interactions between different types of molecules and bare inorganic nanomaterials, offering a perspective to predict the formation of the biocorona. This work aims to stimulate the creation of a new generation of smart nanomaterials that are selective in highly complex environments, and at the same time, that could switch their selectivity depending on the medium properties and the processing steps, in order to separate the whole biomass through the fractionation of valuable products and to design sustainable downstream processes.

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Magnetic Modification of Insect Chitin Material for Various Applications

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Abstract ID #NMM-0274

The creation of magnetically sensitive materials is attracting more and more attention due to the significant potential of the latter in biotechnology, medicine, ecology, engineering, and other fields. Selective magnetic separation from solutions and suspensions is especially important in industrial biotechnological processes and in the treatment of various industrial wastewaters. Magnetic modification is widely used for various diamagnetics. Methods for such modification are constantly being improved [1]. Magnetic modification of natural objects, including polymers, is of particular interest. Chitin is a natural biopolymer that is widely distributed on Earth after cellulose. It is a linear polymer of N-acetyl-d-glucosamine (GlcNAc), structurally similar to cellulose, from which it differs by the acetamide groups at the C2 position of the glucose unit. Using the deacetylation procedure, acid-soluble chitosan can be obtained. With a number of beneficial properties (biodegradability, biocompatibility, non-toxicity, hemostaticity, bioadhesiveness, and immunostimulation) and wide application, the growing demand for chitin and chitosan has stimulated the market to find more sustainable alternatives to the current commercial source (crustaceans). Bioconverter insects such as Hermetia illucens are suitable candidates as chitin is a by-product of insect farms for feed applications. The life cycle of H. illucens consists of five larval stages, followed by prepupal and pupal stages, and adults emerge. Chitin can be extracted from each stage. Thus, the breeding of H. illucens allows a continuous supply of pupal exuvia, part of the exoskeleton released after molting, and dead adults, which are waste products rich in chitin [2]. In our work, various samples of chitosan/sorbents (Lithuania) were obtained from the shells of Hermetia illucens and characterized by SEM, XRD, and TPDMS. Their magnetic modification (nanomagnetite) has been carried out, the possibility and prospects of using them for water purification from organic/inorganic pollutants have been demonstrated.

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REFERENCES

Manipulation of the Domain Structure in Ni₃Pt Nanowires

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Abstract ID #NMM-0288

This work is devoted to the study of the influence of nanowires (NWs) size effects and magnetic field effect applied during electrochemical deposition (ED) on the magnetic domain structure of Ni₃Pt NWs arrays.

Electron-beam lithography in combination with ED was used to fabricate arrays of Ni₃Pt NWs. To study the size effects, several arrays of NWs with different widths (varied from 290 nm to 650 nm) were fabricated on the same substrate. To control the NWs width, electron-beam irradiation dose was changed from 300 to 900 µC/cm² during the lithography process. Except the NWs widths, all other arrays dimensions were kept constant. The area covered with NWs was 0.5×0.5 mm², the length of one NWs was 500 µm, while its height was 150 nm, the distance between NWs was 1 µm. To study the influence of a magnetic field during ED process, two series of samples were prepared: with applied external magnetic field and without it. Magnetic properties were studied with magnetic force microscopy (MFM), and SQUID.

MFM study of 290 nm wide NWs showed the presence of a pronounced periodic magnetic domain structure along the entire length, resembling checkerboard pattern. This arrangement consisted of two domains in the perpendicular in-plane orientation. As the width increases from 290 nm to 650 nm, two chains of magnetic domains move away without changing their volume or inserting additional domains between them. Area between these two chains was left without an MFM contrast.

With a further increase in the width of the NWs to more than 2.6 µm, a transition to a thin-film domain structure is observed. MFM measurements of 340 – 360 nm wide NWs prepared in a magnetic field showed a strong magnetic contrast in the non-magnetic spaces between the NWs themselves. This behavior could be explained by perpendicular, in-plane, domain orientation as well. The magnetic configuration showed a 2D HCP arrangement, and its periodicity was highly ordered over long distances, in contrast to the domains of the sample obtained without the influence of a magnetic field.

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REFERENCES

Spin-Wave Damping in the Presence of Dzyaloshinskii-Moriya Interaction

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Magnonics is a recent scientific field that proposes to use spin-waves for digitizing, processing, and transmission information [1]. It is interesting due to the absence of energy dissipation during spin-waves propagation compared to current electronic devices. For the practical application of functional materials in magnonics, it is important to understand the spin-waves dynamic. It could be controlled via the Dzyaloshinskii-Moriya interaction (DMI) causes by the external electric field [2-3]. Here we show that the DMI modifies the spin waves dispersion in the two-sublattice antiferromagnet structure and makes it asymmetrical concerning the wave vector. Using the phenomenological approach we get analytical expressions for spin-wave spectrum and damping. It is shown that due to the presence of DMI the damping of the right-handed and left-handed spin-waves is different. It opens the possibility to use the polarization of spin-wave as a parameter for encoding information. The obtained results may be important for describing periodic magnetic structures and constructing a spin wave field-effect transistor [4].

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REFERENCES

Annealing Effect on the Structural and Magnetoresistive Properties of Co-evaporated FeNi-Ag Films

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In this work, we synthesized thin-film alloys by co-evaporation in a vacuum from Ni80Fe20 and Ag sources [1]. Structural properties were characterized using a Jeol ARM 200F transmission electron microscope, and quantitative and qualitative composition analysis was performed on an SEM Jeol 7001 TTLS using an Oxford Instruments attachment for energy dispersion X-ray spectroscopy. The samples with a film thickness of 25 ≤ d ≤ 40 nm in a wide range of compositions (0.20 < cAg < 0.72, where cAg is the fraction of silver in the alloy) were studied in as-deposited and annealed states. The results of studies of the structural state, phase composition, and magnetoresistance of the abovementioned samples can be summarized as follows. The phase composition of the as-deposited samples corresponded to fcc-Ni3Fe (where x ≈ 3) + fcc-Ag + solid solution fcc-Ni3Fe(Ag). After annealing at 600 K < Ta < 800 K, the phase composition of the samples corresponded to fcc-Ni3Fe + fcc-Ag. Before annealing, the samples had a structure where permalloy granules with the size L = 6 ÷ 29 nm (depending on the composition) were placed in the silver matrix. Annealing at a temperature of Ta = 700 K led to an increase in the size of the granules (L = 11 ÷ 36 nm) and the formation of permalloy fcc-Ni3Fe clusters due to the decay of a solid solution fcc-Ni3Fe(Ag). The study of magnetoresistive properties showed that as-deposited films were characterized by isotropic magnetoresistance in a wide range of compositions. The field dependences of the magnetoresistance were typical for granular systems consisting of superparamagnetic granules placed in a nonmagnetic matrix. The maximum value of the giant magnetoresistance, measured in longitudinal geometry at Tm = 300 K, was observed in the film with the composition Py0.39Ag0.61 (GMR = 3.15 %) with the sample thickness of d = 40 nm and in the film with the composition Py0.40Ag0.60 (GMR = 0.64 %) at the thickness of sample d = 25 nm. Film samples that have been annealed at 600 K < Ta < 800 K were characterized by anisotropic magnetoresistance in the whole composition range (0.20 ≤ cAg ≤ 0.72). This change in the magnetoresistive properties was related to a change in the structural state of film alloy samples based on permalloy and silver during the annealing process. It was found that film alloy samples based on permalloy and Ag after annealing at temperatures of 600 K < Ta < 800 K can be a promising candidate for magnetoresistive sensor applications.

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REFERENCES

Coherent Coupling of Two Remote Magnonic Resonators Mediated by Superconducting Circuits

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Abstract ID #NMM-0300

Hybrid magnonic systems incorporating superconductivity have recently emerged as a new promising direction that exploits the advantages of magnon excitations for processing quantum information and high quality factor superconducting resonators [1-3]. However, for designing realistic quantum logic operations with magnonics, an important step is to achieve remote multi-magnon interactions that can be embedded in standard circuit quantum electrodynamics modules such as superconducting quantum circuits.

Here, we develop a superconducting circuit platform, incorporating chip-mounted single-crystal YIG spheres, for implementing microwave-mediated distant magnon-magnon interactions [4]. Coherent level repulsion and dissipative level attraction between the magnon modes of the two spheres are demonstrated, with the former mediated by resonant microwave and the latter mediated by propagating microwave. For a single 250-μm-diameter YIG sphere, we achieve a magnon-photon coupling strength of 130 MHz with both the magnon and photon coherence time approaching 1 μs at 1.6 K, corresponding to a cooperativity of 13000. In a two-sphere-one-resonator circuit, we achieve a resonator mediated magnon-magnon coupling strength of 14 MHz in the dispersive coupling regime where the magnon-photon frequency detuning is ten times larger than their coupling strength. We also achieve level attraction of the magnon modes between the two YIG spheres that are integrated on a coplanar waveguide. Our results provide a realistic platform for constructing hybrid magnonic quantum networks at cryogenic temperatures and that can be scaled-up and incorporated into integrated circuits.

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REFERENCES

Electronic & Magnetic Properties of Monolayer and Bilayer Films of Vanadium-based Transition Metal Dichalcogenides 

VX₂ (X=S, Se, and Te)

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Abstract ID #NMM-0301

The semi-metallic two-dimensional Vanadium based transition metal dichalcogenides focus recently an enormous attention due to their intriguing electronic and magnetic properties, as well as due to their possible application in spintronics [1-3]. We present the results of first-principle studies of electronic and magnetic properties of monolayer and bilayer of VX₂ (X=S, Se, and Te). We find that the Vanadium atoms within individual atomic layers are coupled ferromagnetically, while the exchange coupling between V atoms located in different layers is either ferromagnetic or antiferromagnetic, depending on the stacking type of individual layers in the VX₂ bilayer system (T-type and H-type bilayers).

Apart from electronic structure, we also focus on the magnetic properties of these materials and determined the intra- and interlayer nearest-neighbor exchange interactions and the orbital-resolved magnetocrystalline anisotropy energy (MAE) of V atoms. We found that the in-plane MAE originates mainly from the contribution of dxy and dx²-γy² orbitals of V atoms. Based on the mean-field approximation (MFA), as well as on the random phase approximation (RPA), we determined the Currie temperature. Additionally, we also evaluated transmission probability and thermoelectric characteristics of the monolayer and bilayer VX₂ systems [4].

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Nonlinear FMR Linewidth Dependence on Frequency in Strained Garnet Films

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Abstract ID #NMM-0323

We report on the correlation of structural and magnetic properties of Y\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} (YIG) layers deposited on Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} substrates using pulsed laser ablation [1]. The recrystallization of YIG on the lattice-mismatched substrate can result in different film properties when compared to the high-temperature deposition. We observe an unexpected formation of interfacial tensile strain and consequently strain-induced anisotropy contributing to the perpendicular magnetic anisotropy. Moreover, the epitaxial strain has a significant impact on FMR linewidth which is significantly increased in comparison to a film on Gd\textsubscript{3}Ga\textsubscript{5}O\textsubscript{12} substrate. Notably, the linewidth dependency on frequency has a negative slope. The unusual linewidth behavior is explained within the proposed anisotropy dispersion model. Good agreement of experimental findings with theoretical predictions suggests that the anisotropy axis is tilted from the film normal and dispersed. We conclude that the strain homogeneity plays a crucial role in the attainment of narrow FMR linewidths reflecting low magnetization damping of the films.

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Possible Observation of Magnon-Plasmon-Polaritons in the Ka-band

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Abstract ID #NMM-0349

Magnetoplasmonics is an emergent field of applied physics and electronics, which has great potential in medicine, security, communications, and other applications [1]. Surface plasmon-polaritons (or surface electromagnetic waves) and related quasiparticles are well known in optics and terahertz band, however, their systematic study in microwave band was initiated during the last decade [1, 2]. In a recent paper [3] it was shown that the surface electromagnetic oscillations coupled to the magnetization oscillations in the so-called surface electromagnetic wave resonator (SEWR) operating in the X-band can be considered as bias magnetic field-driven microwave surface plasmon-polaritons (MSPPs). In this paper we study the conditions of existence for possible MSPPs in the SEWR placed in the Ka-band rectangular waveguide.

The experiment was carried out by the standard reflectometry method using a scalar network analyzer R2-65 operating in the Ka-band. The ferromagnetic SEWR made of Py has a form of thin plate with sizes: L = 3 mm, W = 2 mm, D = 0.02 mm (resonator thickness). The SEWR was placed in a standard rectangular waveguide, and the waveguide axis was parallel to the Py plate’s plane; W is the resonator size along the waveguide axis. The angle between the SEWR’s plane and the wide wall of the waveguide was chosen ~ 5º.

In the experiment, we measure the reflection of microwave power supplied to the SEWR depending on the longitudinal bias magnetic field created by an electromagnet. We observe a substantial minimum of the reflection coefficient R from ~ 0.9 at zero bias magnetic field to ~ 0.4 at the bias magnetic field Bc ~ 500 mT for the SEWR operating at frequency of 29.8 GHz, while for bias magnetic field exceeding Bc ~ 500 mT coefficient R increases with the field. We believe that the obtained experimental data can be explained by the excitation of MSPPs in the Ka-band. In such a model the frequency of magnetization oscillations excited by an incident microwave signal can be controlled by adjusting the bias magnetic field, and when the frequency of these oscillations (at Bc ~ 500 mT) coincides with the frequency of excited surface plasmon-polaritons, this caused an efficient excitation of MSPPs.

The obtained results can be useful for the development and optimization of microwave and subterahertz frequency plasmonic devices.

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Computing with Spintronic Devices & Probabilistic Bits

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Abstract ID #NMM- 0352

Spintronic technology, which takes advantage from the simultaneous use of charge and spin of the electron, has recently grown attention because of its success stories, starting from the hard disk read heads to the spin-transfer-torque MRAMs, in solid-state devices. A key building block of spintronic devices is the magnetic tunnel junction (MTJ). The fundamental element of a MTJ is a tri-layer composed by two ferromagnets separated by a thin isolating material. The resistance of this tri-layer depends on the relative orientation of the magnetization vector of each ferromagnet. In general, one of the two is designed to be fixed while the other can be manipulated easily with field, current and/or voltage. Together to the switching, it has been shown that in presence of a dc spin-polarized current it is possible to excited self-oscillation of the magnetization having the so called spin-transfer-torque oscillator while with an ac input it is achieved the diode effect. In this talk we will review the fundamental properties of spintronic devices and their applications as hardware building block in neuromorphic computing, in particular for the realization of neurons and synapses. Depending of the MTJ physical and geometrical parameters, it is possible to reproduce sigmoid and ReLU activation functions (most used so far at software level). we also show a possible use of spintronic diodes to implement analog multiplication, which is a key operation in convolutional neural networks (CNN), introducing the concept of degree of rectification (DOR). We will also discuss antiferromagnetic devices for implementation of synapses and memristive systems for computing applications.

In the last part of the talk, I will review our recent results on Ising machines (IMs) and their potential hardware implementation with spintronic technology focusing on oscillator-based IMs and IMs built with p-bits (probabilistic computing).

This computing paradigm is very promising to solve combinatorial optimization problems (COPs), which are a class of mathematical problems that have important applications in a variety of industrial and scientific fields, which span from logistics geoscience from water distribution network design o job scheduling. Many of these, such as maximum cut (Max-Cut), Boolean satisfiability (SAT) or the travelling salesman problem, are NP-complete or NP-hard, meaning in their worst-case instances they have no polynomial-time solution.

We show how the probabilistic computing can be used to solve max-sat instances (the other problems can be mapped on them) beating state-of-the-art solvers having a time-to-solution to 95% at least one order of magnitude smaller.

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Spin-orbit Coupling Related Phenomena in Thin Film Heterostructures

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Utilization of the spin currents is essential in a new class of spintronic devices that can serve as an energy-efficient alternative to conventional electronic memories and computing platforms [1]. Strong spin-orbit coupling existing in a range of materials such as heavy metals, 2D van der Waals structures or topological insulators enables the generation of the spin-polarized current with different symmetries. Such spin current can be used to control the magnetization state of thin film heterostructures leading to the magnetization switching or oscillations by spin-orbit torques (SOT).

In this talk, I will present current trends and challenges in SOT hybrid heterostructures. Primarily I will focus on the unconventional torque symmetries observed in van der Waals heterostructures [2] and low symmetry crystals [3]. Various engineering methods of the thin film structure will be presented to obtain external magnetic field-free magnetization switching, for example, by using antiferromagnets, a combination of spin transfer torque and SOT, and by utilizing interlayer coupling between ferromagnets [4-5]. Finally, I will discuss the potential ways to improve the SOT efficiency for the application in the next-generation non-volatile random access memories.

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REFERENCES

2D and 3D Magnetic Topological Charges: from Skyrmions to Hopfions

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Topological solitons of a vector field describing an order parameter can be classified by using maps from the coordinate space \((r)\) to the order parameter space. The vector order parameter for a ferromagnetic media is its net magnetization \(M(r)\). The magnetization field in 3D space represented by the unit field vector \(m(r_\alpha) = \frac{M(r)}{|M(r)|}\) depends, in general, on three spatial coordinates \(r_\alpha, \alpha = 1, 2, 3\). The theory of topological charges in 1D and 2D space is well developed and used for the classification of topological magnetic solitons such as domain walls (kinks), vortices and skyrmions. Topological charges describe degrees of mappings (homotopy invariants) of 1D (S1) or 2D coordinate space (S2) to the unit sphere \(m^2 = 1\) in the magnetization space \(S^2(m)\), i.e., \(S^1 \rightarrow S^2(m), S^2 \rightarrow S^2(m)\). There is interest nowadays in 3D inhomogeneous magnetization configurations classified by a linking number of the preimages of two distinct points in \(S^2(m)\) on the 3D sphere \(S^3\), i.e., by the Hopf index. The corresponding configurations are called "hopfions". The Hopf index can be represented as some integral of the expression composed by a continuous magnetization field and its spatial derivatives.

A hedgehog or Bloch point is a point-like 3D magnetization configuration in a ferromagnet. Regardless of widely spread treatment of a Bloch point as a topological defect, its 3D topological charge has never been calculated. Here, applying the concepts of the emergent magnetic field and Dirac string, we calculate the 3D topological charge (Hopf index) of a Bloch point in a spherical soft magnetic particle and show that due to the magnetostatic energy contribution it has a finite, non-integer value \([1]\). Thus, Bloch points form a new class of hopfions - 3D topological magnetization configurations. The calculated Bloch point non-zerogyrovector leads to important dynamical consequences such as the appearance of topological Hall effect. The Bloch points constitute an essential part of the magnetization configurations of the Bloch point domain walls in cylindrical nanowires. Therefore, the calculations of the Bloch point 3D topological charge and gyrovector can serve as a benchmark for consideration of the complicated Bloch point domain wall dynamics in magnetic nanowires.

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Novel Sb$_2$O$_3$ and SnO$_2$ Nanoparticles Decorated Talc Pigments for Broadband Electromagnetic Wave Absorption

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Abstract ID #NMM- 0370

The talc pigments were mostly used as a special pigment in the paint, plastics, cosmetics, and the coating industry. However, in this study, the fields of electromagnetic wave absorption were provided to talc particles with SnO$_2$ and Sb$_2$O$_3$ nano-coating. Herein, we report a novel SnO$_2$/talc, Sb$_2$O$_3$/talc, and SnO$_2$:Sb$_2$O$_3$/talc nanocomposites prepared by using the sol-gel method. The phase identifications, crystal structure, and morphological properties of obtained nanocomposites were observed by X-ray diffraction, field emission scanning electron microscope, and Fourier transform infrared spectrometer. The phase, crystal, and morphological examinations of particles confirmed the deposition of SnO$_2$ and Sb$_2$O$_3$ nanoparticles on the talc surfaces. The electromagnetic wave absorption properties of samples were measured using the obtained dielectric and magnetic data. The results show that SnO$_2$:Sb$_2$O$_3$/talc particles displayed higher complex permittivity and dielectric loss values due to the strong interfacial polarization between conductive nano metaloxide shell and talc surfaces. According to the calculated reflection loss values, SnO$_2$:Sb$_2$O$_3$/talc particles exhibited superior electromagnetic wave absorption performance with a minimum reflection loss of -26.1 dB for 2.8 mm thicknesses with effective bandwidth between 8.2-9.8 GHz.

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Heralded Parametric Single Magnon Source

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The creation and detection of single-magnon states constitute an interesting and intriguing challenge for quantum magnonics. An approach using a superconducting qubit paired to a ferromagnet in a volume cavity has already been demonstrated [1]. In this work, we present an all-magnon way to construct a single magnon source [2]. If one considers a uniform microwave pumping field applied parallel to the magnetization direction of a ferromagnet (in our experiments we used a single-crystal Yttrium Iron Garnet film of 5.1 μm thickness), the so-called parallel pumping process could lead to the creation of a pair of magnons at half of the pumping frequency [3]. In a quantum limit, this process is analogous to the spontaneous parametric down-conversion process in quantum optics but offers much more possibilities for control over the generated magnons’ frequency and momentum. In our experiments at room temperature, we use an open dielectric resonator with a resonant frequency of about 13 GHz to enhance the pumping efficiency. When the width of the pumping area is large compared to the wavelength of the generated magnons, they obtain equal, but opposite wavevectors and propagate in opposite directions towards detection antennas. The magnetic field was tuned to achieve optimum generation conditions. A magnon pair is created spontaneously by a pumping microwave photon. Each magnon from this pair is then coherently amplified by the same microwave pumping signal and result in strong multi-magnon signals containing information about the initial pair of magnons. The calculated cross-correlation between two detected in a single-shot experiment signals confirms their creation by the same parametric down-conversion process. In the quantum limit, such a device can serve as a single magnon source if one of the outputs will be used for heralding the generated magnon number.

The described device could be used together with the recent advancements in theory and fabrication [2, 4, 5] to create a variety of devices and circuits, such as all-magnon qubits, quantum gates, and spin-based quantum memory.

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Quantum Magnonics: When Magnon Spintronics Meets Quantum Information Science

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Abstract ID #NMM-0372

Spintronics and quantum information science are two promising candidates to innovate our storage and information processing technologies. For a long time, however, the interplay of these two fields was rare due to the distinct properties of the classical magnetization and quantum bits. Thanks to the recent progress in coding information in magnons, this situation has changed significantly. Furthermore, advances in understanding the entanglement of quasi-particles and in designing high-quality qubits and photonic cavities for quantum information processing make it realistic to integrate magnonic systems with known quantum systems including cavity photons, superconducting qubits, nitrogen-vacancy centers, and phonons for collaborative information processing. These developments have witnessed the birth of quantum magnonics [1], which combines the communities of spintronics, quantum optics and quantum information science.

In this talk, I will give a thorough overview of the basic concepts of magnons and quantum entanglement and discuss the generation and manipulation of quantum states of magnons for quantum information science. In particular, I will focus on the generation and detection of single magnon state in a nanomagnet [2]. In addition, I will present the decoherence channels of magnon quantum states including the relaxation and pure dephasing channels [3]. Performing quantum operations within the magnon coherence time will be crucial for its usage in information processing.

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Curvilinear Magnetism: Fundamentals and Applications

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The behaviour of any physical system is determined by the order parameter whose distribution is governed by the geometry of the physical space of the object, in particular its dimensionality and curvature. In magnetism, the coupling between geometry (topology) of a ferromagnet and magnetic order parameter brings about novel responses of curved thin films and nanowires [1]. In thin film limit, local curvatures can force a geometry-driven local interactions like Dzyaloshinskii–Moriya interaction (DMI) and anisotropy as well as novel non-local chiral effects [2]. In addition to activities on geometrically curved ferromagnets, there are recent appealing developments for curvilinear antiferromagnets where curvature effects results in the appearance of chiral responses, helimagnetic phase transitions, weak ferromagnetism and hybridisation of spin wave modes [3]. Contrary to planar non-collinear structures, curvilinear design enables 3D architectures, which can revolutionize magnetic devices with respect to size, functionality, and speed. At present, 3D-shaped magnetic architectures are explored as spin-wave filters, racetrack memory, artificial magnetoelectric materials, and shapeable magnetoelectronics for human-machine interfaces [4], and soft robotics [5]. These fundamental and application-oriented topics will be covered in the presentation.

REFERENCES

Visualization of the Spatial Displacements of Micro-Magnetic Structural Elements of Ferrite Garnets in an Electric Field

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Changes in the domain structure of thin bismuth substituted garnet films (grown by liquid-phase epitaxy on a (111) Gd₃Ga₅O₁₂ substrates) under joint action of AC and DC electric fields were investigated by the method of optical dark field microscopy [1]. We adapted this method to investigate the influence of an external electric field on the micromagnetic structural elements (in particular, on vertical Bloch lines) of the domain structure of garnets [2]. The effect of changing the image of individual sections of domain walls under specified combined influences is found. In particular, we revealed the magnetoelectric activity effect of vertical Bloch lines as displacements from the regions of their localization. The visual manifestation of the effect strongly depends on the curvature of the domain walls.

Thus, the magnetoelectric effect, as the influence of an electric field on the distribution of magnetization in film samples, was visually observed when a complex influence on the film by the constant and variable (low frequency) electric fields. Our results show the possibility of studying the physics of individual domain walls and their substructural elements at the proposed level of experimental resolution with a combination of magneto-optical, electromagnetic-optical and visual investigations [3]. It is shown that the main cause of magnetoelectric manifestations in ferrite-garnets is the change of the magnetic anisotropy in the electric field.

REFERENCES

Electiv Field Induced Manipulation of Spin Waves

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Spintronics promises to utilize spin degree of freedom of electrons instead of their charge which is used in modern day CMOS-FET based technology for performing Boolean algebraic operations. Among various alternative ideas of non-Boolean algebra in spintronics, wave-based or quasiparticle-based information and computation technology has emerged as one of the most promising ideas. In this regard, the spin waves (SWs), i.e., collective precessional dynamics of spins coupled by short range exchange and long range dipolar interaction in ordered magnetic materials has emerged. To further reduce the power consumption, the spin wave devices must be operated by electric field instead of charge current. The recently discovered voltage- (i.e. electric field) controlled magnetic anisotropy, popularly known as VCMA, can serve this purpose [1]. The electric field applied at the interfaces of ultrathin ferromagnetic films and oxide films can tune interfacial magnetic anisotropy energy through the modulation of electrons population in the 3d orbitals of ferromagnet at the interface.

In this talk I will present how this VCMA can be employed to manipulate the properties of SWs in an efficient manner for the development of all electric field controlled SW based devices, i.e. magnonic devices. VCMA can be used to create virtual nanochannels for SW propagation [2]. The nanochannels can be reconfigured according to the requirements and the properties of the SWs propagating through the nanochannels can also be manipulated. We show that the band structures of the SWs (i.e. magnons) propagating through those parallel nanochannels can also be tuned on-demand by electric field [3]. In absence of gate voltage (i.e. electric field) the magnons show a single mode with typical (flat dispersion) band structure. However, in presence of gate voltage the single mode is split into two creating two dispersive bands separated by a forbidden gap which can be tuned by gate voltage. We further show that the two SW modes propagate though consecutive channels and interestingly they alter their position upon the reversal of gate voltage polarity. VCMA can efficiently tune the frequency of the dipolar-exchange SWs propagating through ultrathin ferromagnetic films [4]. Apart from magnetic anisotropy the damping also decides the performance of many spintronics devices. We demonstrate that the damping in ultrathin ferromagnetic films can be modulated both in linear and nonlinear fashion and explain that the presence of Rashba spin-orbit coupling and the electric field dependence of Rashba strength is the origin behind the observed nonlinear modulation [5]. Notably, the choice of the buffer layer and oxide materials solely decides the weight of linear to nonlinear damping behavior.

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Noncollinear Magnetic Nanostructures as Building Blocks of Topological Magnonic Crystals and Magnetic Force Microscopy Probes

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One of the most attractive features of the 2D topological materials is the presence of unidirectional edge states which are insensitive to defects and impurities. Due to their robust transport properties, these topological edge states are considered potential candidates for information carriers in future spintronic devices. The existence of topological edge states was demonstrated theoretically and experimentally in many wave-hosting systems, e.g. 2D electronic topological insulators or photonic, acoustic, and mechanical metamaterials.

Over the past decade, several theoretical concepts predicted the existence of topological edge states in magnonic systems. However, the experimental demonstration of the topological edge states in the magnonic platform is still missing. The most significant challenges hampering the experimental observation of edge states include e.g. complexity of the sample geometry, control of the ground state, or high density of modes in scaled-up system elements.

Shindou et al. [1] proposed a 2D topological magnonic crystal, with a unit cell consisting of four noncollinear macrospins ordered in a vortex-like ground state. We expand this approach and present a magnonic crystal with a simple geometry, where a unit cell is made of four ferromagnetic triangles of equal shape. We calculate numerically the band structure of a finite strip made of magnonic crystal and identify the bands located in the bulk band gap, which correspond to unidirectional edge states. We show that our magnonic system is a strong candidate for the experimental detection of topological edge states. To control and probe the ground state of the magnonic crystal, the magnetic force microscopy (MFM) technique is one of the most suitable.

Further, based on our rich experimental experience with the implementation of novel MFM methods (e.g. switching magnetization MFM, dual-tip MFM, dual-cantilever magnetometry), we have developed a durable MFM probe with a ferromagnetic disk located at its apex [2]. The noncollinear magnetization of the disk is in a vortex state with the vortex core playing the role of the sharp MFM probe. Such vortex core MFM tip is robust against mechanical deformations while keeping the fixed magnetic moment.

We study theoretically and experimentally the performance of the vortex core MFM probes, optimize their parameters [3], and identify their limitations.

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Linear and Non-linear Out-of-Plane Nano-magnonics

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Abstract ID #NMM-0398

Magnonics addresses the physical properties of spin waves and utilizes them for data processing [1]. Nanomagnonics addresses the investigation of spin waves in magnetic nanostructures of minimal sizes of a few hundred nanometers or less. Previously, only the in-plane magnetized nanostructures were investigated: A single-mode spin-wave propagation with 1.8 µm propagation length was observed in the 50 nm-wide yttrium iron garnet (YIG) waveguides magnetized along [2]. The longer propagation length of 8 µm and the phenomenon of the edge modes merging were observed in the same nano-waveguides magnetized in-plane transversally [3]. The out-of-plane investigation of spin waves in YIG nano-waveguides was beyond the state-of-the-art since the scattering cross-section in the Brillouin Light Scattering (BLS) spectroscopy was expected to be zero in the small precession angle regime [4].

In the talk, I will present a set of experimental and numerical results on the investigation of spin waves in out-of-plane magnetized YIG nano-waveguides. This configuration offered a set of conceptual advantages compared to the in-plane configurations:

– The BLS signal of excited spin waves for out-of-plane configuration appeared to be comparable to that of in-plane magnetization for the same applied microwave power.

– The out-of-plane magnetization allowed for the excitation of extensive precession angles of up to ~50° without triggering parasitic multi-magnon scattering phenomena responsible for the loss of coherent information carried by spin waves.

– A “controllable” nonlinear shift of the dispersion curve up to 2 GHz was observed experimentally and used successfully for the excitation of short-wavelength exchange spin waves. The mechanism of the wavelength transformation down to 200 nm wavelength. This phenomenon allowed for the efficient detection of spin waves at distances of at least 35 µm from the antenna.

– The out-of-plane magnetization allows for the isotropic spin-wave transport in 2D magnonic circuits, one of the critical challenges for the in-plane magnetized networks, and is an ideal configuration for the inverse-design magnonics [5].

On the other hand, out-of-plane magnetization requires the application of relatively large external magnetic fields to overcome the demagnetization. However, the use of nanostructures automatically reduces the magnitude of the required fields, and the novel out-of-plane easy-axis material, like partially compensated Ga:YIG [6], is another step towards application-relevant devices [1].

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Brillouin Light Scattering Measurements of Nanoscale Spin Waves

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Magnonics is a prospective beyond CMOS technology which uses magnons, the quanta of spin waves, for low-power information processing. Many magnonic concepts and devices were recently demonstrated at the macro- and microscale, and now these concepts need to be realized at the nanoscale. Brillouin light scattering spectroscopy and microscopy (BLS) has become a standard technique for spin wave visualization and characterization and enabled many pioneering magnonic experiments. However, due to its fundamental limit in maximum detectable magnon momentum, the conventional BLS cannot be used to detect nanoscale spin waves. Taking inspiration from the tip- and surface-enhanced Raman scattering spectroscopy, nanosized apertures or other plasmonic structures made of metals have been used to locally enhance the electromagnetic field and increase the range of the accessible k-vectors [1, 2]. Unfortunately, the efficiency of the plasmonic approach is severely limited by high optical losses in metallic structures which makes it unsuitable for convenient magnon measurements. However, recent advances in nanophotonic suggest that plasmonic structures made of metals can be substituted by structures made of dielectric materials. Dielectric nanoresonators have an advantage in reduced dissipative losses and associated heating, while their high refractive index still enables comparatively strong light confinement.

In the talk, I will present how optically induced Mie resonances in dielectric nanoparticles can be used in magnonic BLS experiments to increase the magnon signal and to enhance the range of accessible k-vectors [3]. In a series of experiments complemented with BLS signal modelling using a combination of micromagnetic simulation and finite-difference-time-domain electromagnetic field simulation we demonstrate that 200 nm wide and 60 nm thick silicon disk placed on a 30 nm thick permalloy film can increase the thermal BLS signal by factor of 5 and at the same time increase the maximum detectable spin wave k-vector from 10 rad/mm to 50 rad/mm (when compared to the measurement on the bare permalloy film). I will also demonstrate that the approach is universal and works also with coherently excited spin waves. The presented findings elevate BLS microscopy to the forefront of the nanoscale magnonics research and the possibility to probe materials with high momentum photons is relevant also for other applications, e.g. for phononic studies or even mechanobiology experiments.

REFERENCES

Probing Spin Waves in Individual Magnetic Nanoelements

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Abstract ID #NMM- 0404

A series of our recent experiments on individual nanomagnets fabricated using focused electron beam induced deposition (FEBID) will be discussed. First, an original spatially resolved approach for spin-wave spectroscopy of individual circular magnetic elements with sample volumes down to about 10−3 μm³ will be presented [1]. The key component of the setup is a coplanar waveguide whose microsized central part is placed over a movable substrate with well-separated CoFe-FEBID nanodisks which exhibit standing spin-wave resonances. The circular symmetry of the disks allows for the deduction of the saturation magnetization and the exchange stiffness of the material using an analytical theory. Next, using this approach, the engineering of the magnetic properties of CoFe-based nanodisks fabricated by FEBID will be demonstrated [2]. The material composition in the nanodisks was tuned in situ via the e-beam waiting time in the FEBID process and their post-growth irradiation with Ga ions. The achieved saturation magnetization Ms variation in the broad range from 720 to 1430 emu/cm³ continuously bridges the gap between the values of widely used magnonic materials such as Permalloy and CoFeB. Further, nanovolcanoes – nanodisks overlaid by nanorings – will be introduced as purpose-engineered 3D architectures for nanomagnonics [3]. The extension of 2D nanodisks into the third dimension allows for engineering their lowest eigenfrequency with 30% smaller footprints. The nanovolcanoes can be viewed as multi-mode microwave resonators and 3D building blocks for nanomagnonics. Finally, spin-wave phase shifters upon a single nanogroove milled by a focused ion beam in a Co–Fe microsized magnonic waveguide, characterized by all-electrical spin-wave spectroscopy, will be described [4]. By varying the groove depth and the in-plane bias magnetic field, we continuously tune the spin-wave phase and experimentally evidence a complete phase inversion. The proposed phase shifter can easily be on-chip integrated with spin-wave logic gates and other magnonic devices.

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Advances in Nanowire Spin Hall Oscillators

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Abstract ID #NMM- 0409

Spin Hall oscillators (SHOs) are nanoscale sources of electrically tunable microwave radiation and thus are attractive for applications such as wireless communications, neuromorphic computing [1], and microwave assisted magnetic recording [2]. This talk will cover recent advances in increasing nanowire spin Hall oscillator amplitude through device dimensionality [3], magnetoresistance enhancement [4], and engineering of magnetic energy landscape. The advances will be demonstrated through experimental and micromagnetic results. First this talk will cover the dimensional crossover that occurs from quasi-1D to 2D behavior in Pt/Ni80Fe20 nanowire spin Hall oscillators. It has previously been shown that spin Hall current cannot excite coherent SHO modes in quasi-two-dimensional (2D) ferromagnetic films [5], but can excite SHO modes in quasi-one-dimensional (1D) structures. We show that increasing the wire width leads to a larger number of excited SHO modes and a corresponding reduction of amplitude and coherence of each mode. Second, we will show how the output power of spin Hall oscillators can be increased by adding a GMR “amplifier” layer. We will demonstrate that the increase in output power is due to two effects working in concert: 1) Increased magnetoresistance using current in-plane giant magnetoresistance (GMR) rather than anisotropic magnetoresistance (AMR). 2) Matching symmetry of magnetoresistance to symmetry of spin Hall torque. Finally, we will present a new type of SHO engineered to have easy-magnetic-plane oriented normal to the film plane, enabling large-amplitude spin Hall driven dynamics. While many ferromagnets exhibit natural easy-plane anisotropy in the film plane, the spin Hall current in a heavy metal/ferromagnet bilayer is polarized in this plane and thus cannot drive large-amplitude dynamics. We demonstrate that the desired easy-plane anisotropy can be achieved by tuning shape and perpendicular magnetic anisotropies in a simple-to-fabricate SHO nanowire, leading to significantly enhanced microwave emission.

REFERENCES

Low Noise TMR Sensors Utilizing Spin-torque

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Abstract ID #NMM-0433

Magnet sensors with low zero field offset are of utmost importance for various application ranging from current sensors to compass applications [1]. A standard way to reduce the offset is to operate the sensors in a Wheatstone Bridge configuration. However, since all four sensors in such a bridge are never identically an fundamental field offset remains. Within this talk we will present sensors based on spin orbit torque effect that can solve this problem and exhibit extremely low offset. The device consists of a thin heavy metal layer (HM) with a ferromagnetic layer (FM) on top with perpendicular anisotropy ($z$-direction). At equilibrium the free layer breaks up into a multidomain structure. An interesting effect occurs if a current is applied in the heavy metal layer. Due to the interplay of fields in the current direction ($x$-direction) and the damping like torque term an effective field in the $z$-direction occurs. As a consequence, the domain that point in the $+z$ direction grows. The average $z$-component is read out by the anomalous Hall effect in a Hall bar design. If the SOT current polarity is reversed the opposing effect occurs and domains in the $-z$ direction grow. If these two signals are subtracted the sensor signal can be obtained. The measurements show that one can achieve a low offset in the 50 μT range and tune the sensitivity reproducibly by 200-300% which is encouraging for further development of this sensing principle.

REFERENCES

Magnetically – Triggered Protein Release Using Iron Oxide Core – PNIPMAM Shell Nanoparticles

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Abstract ID #NMM- 0437

Superparamagnetic iron oxide nanoparticles (IONPs) are well known for biomedical applications due to their inherent magnetic behaviour and biocompatibility [1]. IONPs can be heated by an alternating current magnetic field (ACMF) and the heat generated can be used in magnetic hyperthermia and drug delivery applications. IONPs functionalized with temperature-responsive polymers present a potential combination for drug delivery and release [2, 3]. Poly(N-isopropylmethacrylamide) (PNIPMAM) is such a polymer that is soluble in water below its lower critical solution temperature (LCST ~ 45°C) but it collapses and becomes insoluble above LCST. Here, the synthesis of Fe3O4 core-PNIPMAM shell nanoparticles is reported along with their potential use as a protein carrier in-situ. The present study could be useful in understanding protein-IONPs interactions which is an essential criterion in designing any protein carrying cargo.

REFERENCES
Imaging Spin Waves in a Low-damping Ferrimagnet with Low Magnetization

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Spin waves have been studied extensively in the past, both from a fundamental point of view and in prospect of their potential application as information carriers in future spintronic logic and memory devices. For most application scenarios, it will be indispensable to utilize short-wavelength spin waves and materials with low magnetic damping. In that respect, ferrimagnetic yttrium-iron-garnet (YIG) stands out with the highest known magnon life time of all materials. Antiferromagnetic materials on the other hand exhibit ultrafast spin dynamics with frequencies up to the THz range, thereby providing potential benefits for fast spin-wave signal processing. We aim at combining these properties by studying sub-micron spin waves in YIG films that are doped with gallium (Ga) in order to approach antiferromagnetic compensation. Such films were grown by liquid-phase-epitaxy on bulk gadolinium-gallium-garnet (GGG) substrates. We directly imaged GHz spin-wave dynamics in these films by time-resolved scanning transmission x-ray microscopy (TR-STXM). For that purpose, we developed a thinning process to reach soft x-ray transmissivity, employing a combination of mechanical lapping and xenon focused ion beam (FIB) etching from the substrate side. Spin waves in the Ga-doped YIG were excited using a lithographically patterned microstrip antenna and they exhibited significant propagation lengths, confirming the low magnetic damping of the material [2]. We observed an almost isotropic spin-wave dispersion, which suggests that the corresponding waves are already exchange dominated, even for wavelengths above 100 nm. This situation can be explained by the large exchange length of the material, as a result of its low net magnetization. In addition, we observed a strong amplitude nonlinearity in the spin-wave excitation process, leading to a local isotropic emission and exceptionally high spin-wave amplitudes, exceeding precession cone angles of 50°. Our results are in line with complement findings from other groups [3, 4].

REFERENCES

In silico Investigations of Magnetic Soft Matter

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Abstract ID #NMM- 0450

In recent years, we observe a rapid development of synthesis techniques that opens up new ways of tailoring magnetic nanoparticles, their size, shape and internal anisotropy. The idea of creating magnetically controllable colloids whose rheological properties can be finely tuned on the nano- or micro-scale has caused a lot of experimental and theoretical effort, but still remains not fully realised. The main challenge on this way is that in systems whose building blocks are ranging between single magnetic nanoparticles to complexes of such nanoparticles bound together by various mechanisms, the classical concept of hydrodynamics breaks and the thermal fluctuations matter as much as the interactions.

In my contribution I will explain how computer simulations can be employed in order to model the behaviour of magnetic soft matter – magnetic nanogels, polymer-like structures, anisometric and anisotropic magnetic particles, aiming at deeper understanding of the key interactions, control parameters and magnetic response [1-4]. Those findings I will put in the context of nanofluidics.

REFERENCES

TRACK 8
“SUPERCONDUCTIVITY IN NANOSCALE & MESOSCOPIC SYSTEMS”
Controlling Dendritic Flux Avalanches by Nanostructure of Superconducting Films

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Niobium Nitrate (NbN) superconducting films are extensively used in superconducting electronics, for example as a material for single-photon microwave resonators [1]. Here we report on direct visualisation of magnetic flux penetration into a NbN thin film deposited by High-Temperature Chemical Vacuum Deposition (HTCVD) [2]. The film is of the thickness of 90.8 nm. It is deposited at temperature of 1200°C on a single-crystal α-Al2O3 (0001) c-axis substrate (sapphire). The visualisation is done by Magneto-Optical imaging [3] allowing to see directly distribution of magnetic flux in the superconductor. It is found that at low temperatures magnetic flux penetrates into the film in the form of dendritic flux avalanches [4]. Moreover, the shape of dendritic avalanches appeared to be very unusual, previously not reported in the literature. The branches of avalanches persistently follow one specific direction in the plane of the film. To clarify the origin of this effect, high-resolution Scanning Electron Microscopy and Atomic Force Microscopy have been used in combination with the Fast Fourier Transform of the obtained images. It was found that the origin of the selected direction in the dendritic flux penetration is deep on the nanometre scale, namely in nano-channels formed by the merging NbN crystallites during their growth. In this way, nanostructure of the film directly controls dendritic flux avalanches in the superconductor. Varying conditions of deposition would allow actively changing superconducting properties of the films.

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REFERENCES

Ideal Diamagnetism in Brain Microtubules

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Abstract ID #SNMS-0027

With mounting evidences of superconductivity in brain microtubules [1], a key experiment to support this would be a nanometer-scale mapping of their magnetic properties. Magnetic force microscopy [2-5] is a convenient instrument to perform such mapping. Previously, it has been used qualitatively resulting in the detection of strong diamagnetic response coming from the in-plane bundles of microtubules [5]. This was preliminary associated with the feature of ideal diamagnetism and therefore superconductivity in the microtubules. Numerical arguments, however, are still absent and it is unclear in what substance superconductivity resides. In order to clarify this, magnetic force microscopy was extended to force spectroscopy. Moreover, the spectroscopy was performed on cross-sections of microtubules investigating them individually. To achieve this, a special technique of sample preparation has been developed allowing orienting microtubules perpendicular to the substrate. The magnetic mapping revealed strong diamagnetism coming from the inside of microtubules. The analysis of recorded force curves has been performed analytically separating magnetic and van der Waals contributions to the signal. Following this, estimation of the signal expected for ideal diamagnetism has been obtained and compared with the signal coming from the microtubules. It is concluded that microtubules display property of ideal diamagnetism.

REFERENCES
Electronic Transport Properties of Nanoscopic Josephson Junctions

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Abstract ID #SNMS-0084

The presentation will focus on hybrid nanostructures realized by combining semiconductor and superconducting materials. In the last decade, such devices have been intensively studied due to the possibility of realization of the topological superconductivity phase. In particular, I will introduce the physics of superconductor-semiconductor-superconductor junctions. I will refer to the fundamental phenomenon of the influence of the magnetic field on the supercurrent flow. I will present the latest experimental and theoretical efforts in supercurrent imaging and measuring the discrete spectrum of Andreev states that carry current in nanoscopic Josephson junctions.
Unconventional Superconductivity in the 2D Electron Gas at the LaAlO$_3$/SrTiO$_3$ Interfaces

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In recent years the LaAlO$_3$/SrTiO$_3$ (LAO/STO) interfaces have attracted growing interest due their broad range of significant electronic properties as well as the possibility to tune the features of the system by using gate potential. It was found that such systems exhibit insulator to superconductor transitions, large interfacial spin-orbit effect as well as signatures of magnetism [1]. These features makes the LAO/STO interfaces an interesting platform for conducting basic research as well as a promising candidate for technological advancements such as the design of novel ultrasensitive sensors with a strong response to small stimuli.

During the presentation we will overview the basic features of the LAO/STO systems focusing on the unconventional superconductivity [2, 3]. In particular, we will present our recent approach to the theoretical description of the origin of the gate-tunable superconducting phase with the domelike shape of Tc as a function of gate voltage. According to our study this effect can be explained as a consequence of the real-space pairing scenario which leads to the extended s-wave symmetry of the superconducting gap appearing in the range of low electron concentrations. As we will show this approach leads to a good agreement with the available experimental data [4]. We will also discuss the influence of electron-electron correlation, and the spin-orbit coupling on the features of the considered system as well as the anisotropy of the critical magnetic field [4,5].

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TRACK 9

“NANOSENSORS & NANODEVICES”
ZnO Nanoparticle Synthesis to Produce Room-temperature UV Sensors by Spray-coating

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Abstract ID #NMM- 0022

ZnO nanowires, are interesting for sensing applications due to their unique charge transport properties related to their quasi-one-dimensional shape. A form of ZnO nanowires, where 4 nanowires are connected at one end and arranged in space perpendicularly to each other are called ZnO tetrapods (ZnO-Ts) [1]. Compared to other forms of nanowires, ZnO-Ts have the advantage of the intrinsic porous formation, due to their morphology a tight packing is not observed during self-formation under ambient conditions [2]. This leads to a better sensor performance in connection to optimal current percolation path and gas permittance, therefore for a sensor preparation simple coating techniques, such as printing or spray-coating can be used, sensors can be manufactured on any substrates.

In this work, using our developed flame synthesis method [3] ZnO nanotetrapods were grown and separated into fractions by their nanowire dimensions. Using a simple spray-coating technique UV sensors were manufactured and tested in controlled atmosphere. UV sensors show fast and high response even at room temperature at low illumination, superior to other ZnO nanoparticle counterparts. Moreover, the influence of humidity was limited, there was a low change in response due to humidity in the widely used range of 30-90% RH. under UV light of 0.31 mW/cm², the current rose to 35.4 μA, 5.2 μA, and 0.5 μA at -5 V for inter-electrode gaps of 5 μm, 10 μm, and 15 μm, respectively. Furthermore, the photocurrent to the dark current ratio (on-off current ratio) was 2959, 1317, and 399 for inter-electrode gaps of 5 μm, 10 μm, and 15 μm, respectively. The fastest rise time demonstrated a sensor with inter-electrode gap of 5 μm – 1.07 s. Sensors with wider gaps were slower: inter-electrode gap of 10 μm – 1.56 s, and sensor with inter-electrode gap of 15 μm – 2.62 s, respectively. The fastest decay time also demonstrated a sensor with inter-electrode gaps of 5 μm – 5.34 s.

In summary, a spray-coating technique was used to create a UV sensors based on ZnO nano-tetrapods. The kinetic sensing response of the measured devices was steady and repeatable. Even at UV irradiation under 0.31 mW/cm² and an applied voltage bias of -5 V, the devices demonstrated an on/off current ratio higher than 2000 and a recovery period of less than 6 s. The discussed spray-coating method of ZnO nano-tetrapods is suitable for sensor preparation on any substrate, therefore it is relevant for flexible UV sensors and enable a variety of usage scenarios. Moreover due to its easy fabrication process and reliable sensing performance at room temperature a wide application prospects can be envisioned.

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REFERENCES

Functionalized Nanodiamond-Rich Interfaces for Biosensing Applications

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Abstract ID #NN-0037

The most common material for electrodes in electrochemical sensing systems is gold or other noble metals, as these can be applied through physical vapor deposition. The recently interesting novel, candidate materials for electrochemical electroanalyses are i.e.: (i) boron-doped diamond (BDD), (ii) high surface area carbon nanowalls (B:CNW), and (iii) composite nanodiamond electrodes.

The novel diamond-rich biosensing surfaces are grown by microwave plasma-assisted CVD. The effect of boron incorporation not only enhances the electrical or electrochemical properties but also influences the structure of electrodes by changing it from the maze-like to a heterogeneous distribution of nearly straight walls. B:CNW or BDD could be nanostructured to achieve microelectrodes.

Both BDD and B:CNW electrochemical electrodes are characterized by outstanding electrochemical properties such as high standard rate constant \(k^\circ\), low peak-to-peak separation value \(\Delta E\) for the oxidation and reduction processes of the \([\text{Fe(CN)}_6]^{3−}/4−\) redox system, and low surface resistivity. For these reasons, B:CNW were successfully applied for primary nucleic acid bases detection or paracetamol determination [1], while BDD electrodes have been used for the development of a rapid-response ultrasensitive biosensor for influenza virus detection [2] stress marker - Isatin determination, or recently for SARS-CoV-2 sensing [3].

Taking into consideration achieved properties, the composite diamond-rich electrodes could be applied in the point-of-care (POC) diagnostic systems, which are currently one of the growing areas of health care. Diamond-based sensors are still not utilized in POCs, while they exhibit much higher sensitivity with price at the same or lower level. Regarding functionality and price of developed diamond sensor technology, it must be noted that such a device will be able to effectively compete with the above-cited products in the demanding markets.

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REFERENCES


“Chimeric” Enzymes: A New Era for Enzyme-based Amperometric Biosensors

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Abstract ID #NN- 0068

Enzymatic polypeptide proteolysis is a widespread and powerful biological control mechanism. Over the last few years, substantial progress has been made in creating artificial proteolytic systems [1], so called “chimeric” enzymes. This triggered the possibility for enzyme-based amperometric biosensors to target analytes that are not involved in ET chains.

In the last decade, the rise of synthetic biology has driven the efforts to construct artificial allosteric protein switches in order to detect such target analytes. Typically, the construction of chimeric enzymes occurs via insertion of a regulatory receptor domain into the biocatalytic reporter domain. Construction of such chimeric enzymes utilizes the recombinant DNA technology that is a core technology of protein engineering [2].

In this regard, we have investigated the bioelectrocatalytic properties of pyrroloquinoline quinone-dependent glucose dehydrogenase fusion with calmodulin (PQQ-GDH-CaM). This protein is catalytically inactive in its ground form but can be activated by the addition of calmodulin binding peptide that induces its conformational transition and activation. This system was practically utilized to realize multipurpose biosensors platforms (e.g., glucose detection, peptide detection, rapamycin etc.) [3, 4].

REFERENCES

Reconfigurable Graphene-GaAs FETs for Digital Electronics

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GaAs is widely used as a channel material in metal-semiconductor FETs (MESFETs) and high electron mobility transistors due to its high carrier mobility [1]. In standard MESFETs, the Schottky diode, which controls the carriers in the transistor channel, has a cut-in voltage of a few hundred mV. Above this value, the forward current of the Schottky diode, i.e., the gate leakage current, increases rapidly, leading to a loss of control over the carriers in the channel and large power dissipation. As a result, it is challenging to realize digital integrated circuits (ICs) comprising standard enhancement mode MESFETs, i.e., MESFETs with a positive threshold voltage (Vth). This is a fundamental requirement for the realization of logic gates that can be cascaded.

In conventional GaAs MESFETs, a fixed Vth is set by the work function of both the metal gate and semiconductor channel during fabrication. In this talk, we will show that it is possible to control Vth of a GaAs MESFET during circuit operation by replacing the conventional metal gate with a monolayer graphene gate. In such graphene-GaAs FETs, the work function of graphene was adjusted by the voltage of an additional Al/AlOx control gate stack fabricated on top of the graphene gate [2]. A variation of the work function of graphene resulted in the modulation of the graphene-GaAs Schottky barrier height (SBH), which set the threshold voltage of the FET. Such effect has previously been used to realize graphene barristors [3] and vertical heterostructures [4].

The modulation of the SBH allowed to convert depletion mode FETs (i.e., FETs with a negative Vth), into enhancement mode FETs. The increase of Vth also increased the cut-in voltage of the gate Schottky diode and, therefore, allowed the use of the FETs under larger gate voltages without increasing the gate leakage current. The fabricated FETs were integrated into depletion-load inverters which exhibited a positive switching threshold when the driver transistor was run in the enhancement mode. This overcomes the problem of cascading conventional depletion mode MESFETs in logic gates and paves the way for novel ICs exhibiting additional functionalities.

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REFERENCES

Highly Sensitive Printed Phototransistors with Liquid-Phase Exfoliated GaSe Nanoflakes

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Abstract ID #NN-0088

Gallium Selenide (GaSe) is a p-type two-dimensional (2D) III-IV semiconductor hexagonal crystal system [1]. Owing to its high photoresponsivity, high on-off ratio, and diverse quantum confinement, it has drawn a lot of attention in electronic and photonic device applications. Along with, GaSe, with its outstanding non-linear optical properties, is a promising candidate for the second harmonic generation and light frequency conversion [2, 3]. Correspondingly, the aim of this study is to introduce a low-cost methodology to fabricate GaSe-based printed phototransistors.

In this study, 5 mg of GaSe crystal sheets and 1 mg polyvinylpyrrolidone (PVP) powder were immersed in a solution composed of 5 ml propanol, 2.5 ml ethanol, and 2.5 ml de-ionized water. Following, the mixture is sonicated for up to 12 hours in an ultrasonic bath. Afterward, the GaSe-based solvent was spin-coated on a Si wafer with a 250 nm oxide layer, while the backside of the Si substrate was already coated with a thin Au layer. It was environmentally annealed at 70 °C for 3 minutes. The top metal contacts were patterned on top of GaSe:PVP coated SiO2/Si/Au substrate by using Ag ink and utilizing an inkjet printer (Suss MicroTec Pixdro Lp50). For the optical characterization, Raman and photoluminescence (PL) spectra analyses by using a 532 nm laser source with low power settings were performed. Raman modes of GaSe nanoflakes appeared to be at the points of 132, 210, 245, and 305 cm-1, which are also compatible with the literature [2, 4]. The PL spectrum was observed at 622.4 nm with a high intensity, which corresponds to the direct transition of direct free exciton of GaSe. To characterize the phototransistor behavior, current-voltage (I-V) measurements were performed by the four-probe method, using a Keysight 2902A precision source measure unit. The measurements were taken in two lighting conditions: with light illumination and in complete darkness. The sun-light simulator consists of a self-made LED-based set up with a daylight spectra illumination, which is very similar to sun spectra. The mobility of the fabricated GaSe-based phototransistor was calculated as 0.64 cm2/Vs at Vd = -3 V and 0.26 cm2/Vs at Vd = 3 V under dark conditions. Also, it was computed that the saturation current corresponds to 50 µA. The photocurrent (Iph) reached up to 14 µA under the light illumination.

In conclusion, the electronic and photo-responsive properties of multilayer GaSe nanoflakes have been studied. The results indicate that GaSe-based phototransistors show a p-type operation with high mobility at reverse-biased voltage. In this study, we proposed a simplified and low-cost process flow for fabricating GaSe-based printed phototransistors for optoelectronic device applications.

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REFERENCES

Enhancing the Performance of All-inorganic LEDs with CdSe-CdS Core-shell Nanorods

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In the past few decades, core-shell heterostructure of nanorods (NRs) has drawn extensive attention due to their low-cost synthesis, high-reaching photoluminescence quantum yield (PLQY), improved efficiency as well as easily tunable emission wavelength, to fabricate all inorganic light-emitting diodes (LEDs) [1]. On the contrary, all-inorganic LEDs are developed frequently due to better device stability in the air [2]. However, NR-LEDs also face many challenges to reach high efficiency i.e., deterioration of electroluminescence, non-radiative recombination, relatively low external quantum efficiency (EQE) compare to organic LEDs (25%) etc. Improvements to these issues will make them ideal candidates in optoelectronic devices [3].

Herein, the aim of this project is to develop highly efficient NR-LED based on multilayer CdSe-CdS dot in rods (DiRs) nanocrystals (NCs). The red emitted CdSe-CdS NRs are synthesized using the ‘Hot Injection’ route and later high-quality core-shell layers are acquired simply by spin-coating core-shell NRs solution directly on hole transport layer (HTL). NiO and Zinc Magnesium Oxide (ZMO) NCs layer are selected as HTL and electron transport layer (ETL) to get balanced charge injection. The NR-LEDs with ultra-pure red emission of 630 nm exhibit a narrow full-width half maxima of 20 nm, low-turn on voltage of 2.2 V and maximum PLQY of 40-60%. Such good results are accountable to the CdSe-CdS core-shell structure with relatively high PLQY and the rod structure specially minimized for the non-radiative energy transfer between closely packed NRs in emissive layer of LED [4].

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REFERENCES

Detection of Agri-Food Chemicals with a Surface-Enhanced Raman Scattering Paper-Based Sensor

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During the last decades, Surface-enhanced Raman scattering (SERS) has proven to be one of the most promising analytical techniques for application in chemical, material and life science, providing good advantages for trace detection in diagnostic and agri-food applications [1]. In fact, SERS combines the chemical ‘fingerprint’ capability of the Raman spectroscopy with the enhancement of Raman signals (up to 1012) associated to the presence of plasmonic surfaces. While different mechanisms have been proposed to explain the SERS enhancement, two contributions are considered the most accepted: chemical effects (CE) and electromagnetic effects (EM) [2]. Different nanostructures can be synthesized as substrates for SERS purposes; in particular, gold spherical nanoparticles, gold flower-shaped nanoparticles, silver spherical nanoparticles and silver nano-prisms have been synthesised for this study.

Food safety has been an increasingly relevant topic in recent years, considering the public health impact, and research has been shifting to focus on point-of-care tests (POCT), for fast monitoring and preventing/control strategies, in opposition to the well-established techniques such as liquid and gas chromatography, polymerase chain reaction (PCR) or enzyme-linked immunosorbent assay (ELISA) [3].

Considering the increase in demand of POCT in different situations, the aim of this work is to fabricate a low-cost, flexible and recyclable SERS sensor, usable in-situ with a good sensitivity. This allows to move away from the common solid substrates, which have advantages in terms of fabrication and precise control of the location and dimension of the plasmon-generating structures but disadvantages, such as cost, flexibility, and difficulty to use them on-site or outside the laboratory [4]. Because of it, our interest has been focused on paper substrates, which offer versatility of analysis and low cost. Selected nanostructures have been deposited in different types of paper substrates by direct-writing method, using a commercial pen, in particular a fountain pen with a medium size nib.

Before ‘writing’, the colloidal solutions are centrifuged and washed to create “nano-inks”, concentrated nanoparticle suspensions, that once deposited on paper substrates, will lead to strong SERS effects, due to their close proximity to each other. At the same time, concentrating the colloidal solutions helps to obtain a higher viscosity, simulating the usual fountain pens inks without addition of further chemicals. Standard Raman probe molecules, such as crystal violet (CV) or 4-aminothiophenol (4-ATP) are used to study the performance of SERS on different substrates and different nanostructures. The final application will be developed for the agri-food sector, for the detection of food contaminants (e.g. antibiotics, pesticides, etc.).

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Growth Kinetics Modeling of Size and Shape Controllable Gold Nanoparticles for the Development of Immunochromatographic Assay

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Abstract ID #NN- 0218

Gold nanoparticles (AuNPs) of different shapes and sizes represent significant color changes in a reaction mixture that act as a promising biosensing tool to develop the rapid Lateral Flow Immunochromatographic Assay (LFIA) [1]. Herein we report that the growth transformations of AuNPs are a function of physicochemical reaction parameters. Surface Plasmon Resonance of anisotropic nanoparticles is dependent on their morphological features and geometry. In this study, we have synthesized the seedless AuNPs by using various molar ratios of HEPES and HAuCl₄. The shape and the geometry of the gold nanostructures were modulated under the influence of pH (5, 7, and 9) of the HEPES, molar concentrations of HEPES to HAuCl₄, and temperature ranges (20 °C, 40 °C, and 60 °C). The change in the color of reaction mixtures over time was recorded in terms of the absorbance of the UV-Visible light in the range of 300-900 nm of the light wavelength. The scanning transmission electron microscopic images employed that the gold nanostructures exist in various shapes and corroborate with the UV-Vis spectrum. It was confirmed that the nano-moieties are anisotropic, stable, and exist in the size range of 1 nm to 100 nm. The present study confirms that the change in the color of nanostructures reactions mixtures is a function of the surface plasmon resonance bands under the influence of physicochemical reaction conditions. Physicochemical parameters such as temperature, pH, and the molar concentration of the reactants act synergistically to influence the reaction kinetics, molecular mechanics, and enzymatic catalysis that aid to affect the size, shape, and biochemical corona of nanoparticles. The findings of the present study explain the growth kinetics of the AuNPs of various colors that can be observed by unaided eyes and have promising applications for the development of the rapid LFIA for the detection of mycotoxins in food samples [2].

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Printed Magnetic Field Sensors: From Wearable Devices to Interactive Surfaces

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Printing electronics is developing as an on-site fabrication approach to obtaining customized functional devices. In particular, printed devices can be designed to suit the specifications of each user, e.g. size, location, and functionality. Our research focuses on developing touchless devices that interact via printed magnetic field sensors. Here we will show our approach to fabricating magnetoresistive printable pastes containing magnetosensitive particles embedded in a polymeric binder. The engineering of the printed sensors relies on the properties of the paste fillers, binder, substrate, and processing techniques.

The properties of the fillers change the output response of the printed sensors. For example, flake particles showing anisotropic magnetoresistance and giant magnetoresistance have excellent sensitivity below 1 mT making them attractive for wearable and on-skin applications. On the other hand, we studied the capabilities of bismuth-based printed sensors showing non-saturating large magnetoresistance; the output characteristics of these devices made them attractive for wide-range magnetic field sensors.

Tuning the mechanical properties of the binder gives special deforming capabilities to the printed sensors. Polymeric binders used to print our sensors on flexible foils allowed us to laminate our printed systems on objects with complex geometries and even on the human skin. For instance, we achieved stretchable (100% strain) magnetic field sensors by using a styrene-butadiene-styrene block copolymer as a binder. We demonstrated that these printed sensors are functional after bending to 16 µm bending radius.

We demonstrated the scalability of printing magnetic field sensors using automatized dispenser printing and laser sintering. This technique offers large-area, affordable, customized fabrication of flexible fully printed magnetic field sensors with minimal material requirements. Such fabrication capabilities open the path for extended interactive smart surfaces and touchless terminal boards. We foresee further developing flexible printed touchless devices in 2D and even 3D printed fully embedded systems for navigation, gaming, personal dosimeters, and health monitoring.

REFERENCES

Flexible Piezoresistive Sensors Based on 3D Graphene Structures

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Abstract ID #NN- 0232

Monitoring the behavior of load-bearing elements in automotive, aviation, aerospace, and construction is crucial for long-time operations [1–4]. For structural health monitoring (SHM), the vibrating wire [3], optical [3, 4], or piezoresistive [2, 3] sensors are commonly used. Among them, the highest potential application shows piezoresistive ones due to very high sensitivity and the possibility to work under low voltages (below 5V). Moreover, this kind of sensor can be mounted on the element surface or integrated into its structure, which does not change the properties of the final composite element significantly, especially considering mechanical properties [2, 4]. Many different piezoresistive materials can be used, but the most promising ones are carbon nanostructures due to their high conductivity, density similar to the polymeric matrix, and positive impact on mechanical properties [5].

Graphene can exist in various forms, classified as 0D, 1D, 2D, and 3D [6]. Three-dimensional graphene is a nanostructure based on two-dimensional sheets of graphene connected in a porous network [7, 8]. Compared to materials of other dimensions, it is distinguished by its empty structure resulting from the interconnected architecture. The 3D version of graphene possesses all the properties of the 2D one; it shows good electrical conductivity and mechanical integrity. Regarding the empty space, it offers an increased surface area while reducing weight (the 3D graphene structure is lighter than graphite) [8].

This study aimed to investigate the effect of graphene amount and its 3D organization on the piezoresistive response of the composite thin film using polystyrene as a polymer matrix. The 3D graphene shells were used as a filler, while the commercial graphene nanoplatelets were used as reference material. Four different amounts of fillers (0.25%, 0.5%, 1% and 2%) were dispersed in ethyl acetate to dissolve the polystyrene. After dissolving of polymer granules, the mixture was mechanically stirred and subsequently solution-cast on glass plates. The filler dispersion in prepared polymer matrices was investigated by means of scanning electron microscopy(SEM). The crystalline structure was studied by X-Ray diffraction (XRD), and thermal properties were characterized by differential scanning calorimetry (DSC). The DC electrical conductivity of graphene-polystyrene composites was measured using a precision LCR meter. The piezoresistive response was measured under finger tapping excitation to determine the composite’s best amount of carbon nanostructure.

REFERENCES

Magnetic Electronic Skins for Self-Supervised Origami Soft Actuators

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Abstract ID #NN- 0236

Soft actuators are coming closer to the capabilities of biological mechanical systems [1]. Biomechanics rely on soft, reconfigurable, and efficient structures that allow the movement, displacement, and interaction of biological systems with their environment. Among others, magnetic soft actuators excel due to the untethered actuation via electromagnetic fields [2]. Such electromagnetic actuation can be controlled via permanent magnets or coils. Alternating magnetic fields combined with the smart design of soft actuators have achieved 100 Hz actuation speeds which are attractive to quickly react and adapt to environmental conditions [3]. Additionally, magnetic origami-like actuators can be specifically magnetized to achieve more complex shape morphing [4].

To close the loop between the actuation of soft systems and the control of their movements is needed a suitable sensing unit. Robotic systems are normally integrated with sensing awareness to interact with their surroundings. Flexible sensors mechanically conformal with soft actuators are still under research development.

Here, we show the first adaptation of magnetosensitive skins laminated on magnetically actuated soft actuators [5]. Ultrathin conformal magnetic field GMR and Hall effect sensors were used to detect the magnetization state, the orientation, and the folding state of origami-like actuators. The magnetic origami foils were made of NdFeB microparticles in PDMS. We found the best thickness and concentration parameters to achieve untethered magnetic folds defined on the fly. We demonstrate the synergistic combination of magnetic soft actuators and e-skins allowed self-guided assembly into a box and boat-like layouts. The assembly process was followed and controlled by the signal recovered from the laminated sensing e-skins. We expect further alike integrations for autonomous remote soft mechatronic systems, where untethered actuation is needed.

REFERENCES

Multi-band Radiation Detector Based on Ag₂O-HgCdTe Composite Structure Formed by Ion Implantation

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Abstract ID #NN- 0325

Multispectral detectors are based, as a rule, on different physical phenomena, and these different phenomena cannot be implemented with one material. For multispectral IR - detectors, several materials are commonly used, each responding to a different wavelength range. Another approach is based on a combination of filters, i.e., on a spectral selection of radiation. At the same time, it would be desirable to have detectors based on a small number of available material technologies or even on one material. One of such materials can be the ternary compound HgCdTe, the bandgap of which can be varied by altering the composition from 1.6 eV for x = 1 to 0 eV for x ≈ 0.165. It is a good material for multispectral IR- photon detectors development and is promising for THz and sub-THz photonics. A commonly used method for the fabrication of HgCdTe-based IR detectors is ion implantation. The advantages of this technique in producing a uniform and shallow junction are recognized. Besides, it is a very powerful tool for the synthesis and modification of the solid-state low-dimensional and nanoscale composite structures.

In this work, we consider the ion-synthesized composite structure Ag₂O/Hg₁₋ₓCdₓTe (x ~ 0.223) as a candidate for multispectral (IR and sub-THz) detection system and present a new mechanism for sub-THz radiation detection with its help. The study results of the composite structures based on nanosized silver oxide inclusions in the semiconductor matrix HgCdTe are presented. HgCdTe layers were implanted with the silver ions Ag⁺. Modification was performed using the method of oblique-incidence (θ = 30°, 45°) ion bombardment. It should be noted that the implantation of the HgCdTe epilayers with Ag ions at the oblique-incidence geometry (45°) gives rise to the metal-oxide nanophase (cubic Ag₂O) precipitation in the subsurface (<100 nm) region of the host material. The surface morphology of (111) Hg₁₋ₓCdₓTe (x ~ 0.223) epilayers due to ion irradiation with energy 140 keV and fluency 4.8x10¹⁵ cm⁻² at T = 300 K was studied. The methods of low-temperature photoluminescence, Raman, and surface photovoltage spectroscopy techniques were used for the sample’s investigation. The observed photosensitivity indicates that the ion-synthesized Ag₂O/Hg₁₋ₓCdₓTe (x ~ 0.223) composite system, in which a metamaterial absorber is integrated directly into the MWIR semiconductor, may be a candidate for multiband detectors. The impedance spectroscopy results have shown the passive inductive properties of the composite structures investigated. We present a new mechanism for sub-THz radiation detection with its help. The photonic properties of the synthesized semiconductor composite structure are discussed in the frame "antenna efficiency" paradigm based on using a metamaterial unit cell as the electrically small, near-field resonant parasitic antenna.
ZnO-Schiff Base Composites for Optical Detection of Cu Ions

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Optical sensors of metal ions today are an important promising direction in the environmental protection industry. The main requirements for the sensor are high sensitivity and selectivity. Schiff bases are complex organic compounds with specific groups. The most important property of the Schiff bases is to host different metal ions. The affinity of the Schiff bases to different ions can be chemically tuned. Schiff bases require nanostructured template to improve sensitivity to the metal ions. ZnO nanostructures have advanced optical properties (room temperature photoluminescence at 378 and 530 nm). Optical emission of ZnO overlaps with optical absorption of Schiff bases, what can induce new optical properties and change electronic structure of Schiff bases.

In this work, we report on modifying of optical and sensitive properties of Schiff bases by integrating with ZnO nanostructures. Sensor tests to Cu\textsuperscript{2+} ions have been performed. ZnO nanoparticles and Schiff base were added to chloroform and stirred for two days. The resulting compound was washed with methanol and dried in vacuum for 24 hours. Structure properties of the ZnO/Schiff base nanostructures have been investigated by SEM, FTIR, diffuse reflectance and photoluminescence (350-800 nm). The presence of the Schiff base of the structure led to a redistribution of emission bands in the photoluminescence spectrum of ZnO. The sensitivity of the resulting compound to copper ions was studied. ZnO/Schiff base nanostructure successfully synthesized, optical and structure properties were studied. The sensitivity of the obtained compounds to Cu\textsuperscript{2+} ions was determined.

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**WS₂ & MoS₂ from 3D to 1D Structures: Curvature and Chirality Induced Properties of Nanotubes**

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Abstract ID #NN- 0358

Wide investigation of multiwall inorganic nanotubes (INTs) of WS₂, a member of the 2D transition metal dichalcogenide (TMD) family, became possible due to the breakthrough in their vapor-gas-solid synthesis, resulting in pure phase and macroscopic amounts [1]. An advance in extremely complicated synthesis of INT-MoS₂ by vapor-gas-solid reaction of Mo oxides with H₂/H₂S gases [2] will be presented as well. These nanotubes demonstrate unique properties due to their nanosize, closed-cage arrangement of the layers into chiral tubes and mechanical strength. Thus, bulk photovoltaic effect (BPVE) was recently discovered in INT-WS₂ [3]. The photocurrent in the nanotube-based device was orders of magnitude larger than in other BPVE materials. The BPVE does not require p–n junctions of traditional photovoltaic effect (PVE) for generation of electric current, and occurs due to the intrinsic properties of INT-WS₂: small band gap (1.4-2.1 eV), broken inversion symmetry and polar structure. This progress is particularly important for environmentally benign energy harvesting because the efficiency of PVE has been almost reached the theoretical limit. An exponential increase of the resistivity with tensile strain was demonstrated up to a recorded elongation of 12 %, thereby making INT-WS₂ suitable for piezoresistive sensor applications [4]. Low temperature cathodoluminescence of single-wall few nm diameter WS₂ nanotubes, produced by high-power plasma irradiation of multiwall WS₂ INTs, demonstrates blue shift, evidencing quantum confinement and strain effect [5]. Bandgap engineering via size and number of layers control in these INTs will be discussed. Recent theoretical calculations demonstrated that mechanical properties of MoS₂ are superior to that of WS₂, as well as their excitonic emission. Therefore, the availability of new MoS₂ semiconductive nanotubes will enable their wide investigation, which anticipates to reveal intriguing applications in the field of photovoltaics and optoelectronics.

**REFERENCES**


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A Free Standing Mechanoluminescent Polystyrene/ZnS:Mn Composite Thin Films for Optical Sensing Application

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Abstract ID #NN- 0362

Mechanoluminescence (ML) is a light generation with the effect of applied mechanical force. The phenomenon is not new but has already been studied by many researchers [1]. Approximately, 50% organic and 60% non-organic materials are mechanoluminescent in nature [2]. ZnS:Mn is a non-organic phosphor material and one of the brightest Mechanoluminescent materials. Due to the lack of understanding in device fabrication, ML sensors are still not part of the market[3-5]. Present work focuses on the development of Polystyrene (PS) and ZnS:Mn based composite thin films. Polystyrene was chosen as it is optically transparent and does not interfere with the optical emission of the phosphor material. The film fabrication is done using the drop-casting method. The fabricated films are free-standing in nature. The films are characterised using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Photoluminescence (PL) analytical techniques. Further, the composite films are tested for the ML characteristic using a customized pressure pulse generator. The pressure range for testing is set from 40bar to 400bar [6]. The obtained results clearly show that the composite films are ML in nature. The ML is in a linear relationship with the applied pressure as proposed by the theory. These films have a tendency to be utilized for the self-triggered light emission optical sensor matrix material in the areas like Aeronautical, civil structure health monitoring and defence application.

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REFERENCES

Thermal Interface Materials for Heat Distribution in Nano-CMOS 3D ICs

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Abstract ID #NN-0411

3D integration is a promising solution to meet the challenge of rising system requirements: better performance, increased functionality, improved energy efficiency, higher bandwidth, better yield and reliability, and a smaller footprint. One of the most promising 3D Integration technologies is 3D stacked ICs (3D SICs), fabricated by vertically assembling multiple electronic chips and connecting them with Through-Silicon Vias (TSVs) into an integrated device. Thermal management of 3D SICs, however, is even more challenging than for 2D due to higher power density and the lower surface-to-volume ratio of 3D structures. Various techniques have been proposed to address the thermal issues of 3D ICs, including advanced materials like carbon nanotube and graphene to help spread the heat and novel cooling technologies such as heat pipes and cooling microchannels. Graphene, a more recently discovered allotrope of carbon, exhibits extremely high thermal conductivity, but simulations suggest multilayer heat spreaders may be technologically more feasible than single-layer graphene. Floorplanning of chip modules into 3D physical geometric arrangements allows for optimization between performance, temperature, and power consumption. It is also an excellent physical stage platform for numerical evaluation of the influence of various advanced thermal interface materials (TIMs) and additional layers of heat spreaders, intermediate materials (IL). In this talk we will discuss 3D IC configurations with three different TIM and IL materials including monolayer graphene, graphite, and copper of varying thickness. We will present and discuss numerical results of the influence of heat-spreading materials on horizontal temperature distribution and vertical thermal gradient in several benchmarks of 3D IC systems. We will outline the need for new nano-materials to improve heat distribution and removal. A short summary of potential candidate materials such as thermal metamaterials, exhibiting thermal properties that do not exist in nature, will be presented.
TRACK 10

“NANOMATERIALS FOR ENERGY & ENVIRONMENT”
Mechanical Spectroscopy of SiO₂/Si, Nanocomposites of Multiwalled Carbon Nanotubes and Polyamide, Polyethylene, Polyvinyl Chloride, and Porous Polystyrene

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Abstract ID #NEE-008

Defect annealing leads to a change in the shape of the internal friction (IF) temperature spectrum Q-1(T) [1]. IF method allows setting the spectrum of structural defects on the analysis of positions of maxima of IF, on the duration of relaxation time τ, and on their deposit in attenuation of elastic vibrations [2].

In this work, a non-destructive method for the technological control of the structure defects by measuring IF temperature spectrum Q-1(T) was used. Ultrasonic (US) pulse-phase method using USMV-LETI, modernized USMV-KNU, and computerized “KERN-4” with frequencies f ≈ 1 MHz and f⊥ ≈ 0.7 MHz, US invariant-polarization method for determining the effective acoustic μ and elastic constants Cijkl were used [3, 4]. The study of the influence of structural defects on damping of vibrations in Si/SiO₂ wafers by the diameter of D = 100÷60 mm and by the thickness of hSiO₂ ≈ 600 nm, hSi ≈ 470 000 nm allows estimating the degree of perfection of crystalline structure. After X-ray irradiation, outcomes of the evaluation of dynamic characteristics of interstitial atoms Sij, vacancy V, and O-complexes were applied for the account of a condition of annealing with the purpose of deriving specific structural defects in SiO₂/Si wafer-plate. The non-destructive method, which allows determining from internal friction difference ∆Q-1/Q-10 of elastic vibrations structure defects density N and the depth of broken layer h, is offered for SiO₂/Si wafer-plates. The quasi-longitudinal US velocity V \([001]\) = 5870 m/s, elastic modulus E[001] = ρV \([001]\) = 80.28 GPa for SiO₂/Si from the oscillogram were determined. Temperature dependence of internal friction Q-1(T) in SiO₂/Si wafer-plate p-type, doped with B, KDB-7.5(100) diameter D ≈ 76·10⁻³ m, thickness hSi ≈ 460-103 nm with SiO₂ layer thickness hSiO₂ ≈ 100 nm after X-ray irradiation with dose Dγ ≈ 102 Gey is showed.

The growth of internal friction maximum height QM-1 indicates the growth of the structural defects concentration n, and the broadening of internal friction maximum QM-1 here represents the relaxation process of structural defects new types in SiO₂/Si wafer-plate. It was found that as the result of the structural defect, annealing IF background QO-1 significantly decreases during measuring of IF temperature dependence Q-1(T), which indicates the improvement of SiO₂/Si crystal structure. The elastic modulus E, the shear modulus G, Poisson coefficient μ, IF Q-1 are dependent on SiO₂/Si wafer-plate anisotropy. The value of IF background Q-10 after temperature T, mechanical treatments describe the changes of the elastic stress σ fields in SiO₂/Si wafer-plate. The study of vibrations of disk wafer-plate Si/SiO₂ at different harmonic frequencies f₀, f₂ made it possible to develop the technique for determining the structural defects density nD for semiconductors.

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REFERENCES

Facile Synthesis of Dopant Assisted MgO-Mg(OH)$_2$ Nanocomposites for Room Temperature Carbon Dioxide Capture

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Carbon capture and storage has long been considered a vital technology for reducing climate change-related greenhouse gas emissions, particularly carbon dioxide (CO$_2$). Many solutions have been proposed to address this problem, including the use of adsorbents that can capture CO$_2$ under various conditions. Magnesium oxide (MgO)-based sorbents have been identified as promising sorbent materials with the potential to improve CO$_2$ capture capacities through a variety of methods. When CO$_2$ is adsorbed, however, the creation of magnesium carbonate (MgCO$_3$) remains a concern because it covers the adsorption surface, causing the rate of adsorption to drop dramatically over time. We engineer the equilibrium of CO$_2$-phobic (Mg(OH)$_2$) and CO$_2$-philic (MgO) phases to break the MgCO$_3$ blocking film, inspired by the alternative hydrophobic and hydrophilic surface morphology utilized by desert beetles in inhibiting the formation water thin coatings that deactivate the hydrophilic sites. In this study MgO–magnesium hydroxide (Mg(OH)$_2$) nanocomposites doped with chloride (Cl-) were synthesized at room temperature utilizing an electrospinning approach followed by hydration via vapour steaming. The sorbent materials were synthesized by doping 5% and 10% Cl- and then exposing them to vapour steam for 15 to 20 minutes at 100 °C, resulting in flower-like nano structures. XRD, SEM, and FTIR analysis were used to characterize the materials' structural and morphological features. TGA analysis was used to determine the CO$_2$ capture capacity of the materials at 100% pure CO$_2$ conditions at 30 °C. When exposed to vapour steam, the production of Mg(OH)$_2$ caused morphological alterations with the creation of flower-like structures. It was apparent that the dopant aided CO$_2$ adsorption performance at room temperature utilizing an electrospinning approach followed by hydration via vapour steaming. The sorbent materials were synthesized by doping 5% and 10% Cl- and then exposing them to vapour steam for 15 to 20 minutes at 100 °C, resulting in flower-like nano structures. XRD, SEM, and FTIR analysis were used to characterize the materials' structural and morphological features. TGA analysis was used to determine the CO$_2$ capture capacity of the materials at 100% pure CO$_2$ conditions at 30 °C. When exposed to vapour steam, the production of Mg(OH)$_2$ caused morphological alterations with the creation of flower-like structures. It was apparent that the dopant aided CO$_2$ adsorption performance at room temperature. The CO$_2$ capture capacity increased by 25-40% depending on the steam exposing time, and the addition of dopant increased the capture capacity even more. The reduced carbonate blocking effect caused by Mg(OH)$_2$ production may have benefitted the Cl- doped MgO-Mg(OH)$_2$ adsorbents' increased CO$_2$ adsorption at room temperature. Moreover, this study opens new opportunities in developing improved yet cost-efficient adsorbents based on MgO for CO$_2$ capture and storage at room temperature.

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Nanocomposite Based on Natural Zeolite Containing Hydrated Iron (III) Oxide for Removal of Heavy Metal Ions From Water

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Synthetic materials, such as hydrated oxides of multivalent metals and composites based on them, are used mainly as sorbents [1] and modifiers of the polymer [2, 3] and ceramic [4] membranes for baromembrane [2] and electrodialytic separation [3, 4]. Sorbents of natural origin are also attractive for practical applications since their synthesis requires no material, labor, and energy costs.

The aim of this investigation is to develop a synthesis method of the nanocomposite, its investigation, and testing for the removal of heavy metal ions from water.

The theoretical approach, which allows us to control the formation of aggregates incorporated into porous matrixes has been developed and verified. The important parameter is the pH of a precipitator: the higher this value, the larger aggregates are formed. Based on the approach, a method of obtaining the composite based on natural clinoptilolite-based zeolite containing nanoparticles of hydrated iron oxide has been developed. The sorbents were investigated using XRD, TEM, SEM, and porometric methods.

A weakly basic precipitator has been recommended in order to obtain the nanosized aggregates of the modifier. During the synthesis, the porous structure of the zeolite substrate is transformed: highly ordered pores, a radius of which is 1-2 nm are unblocked. This is due to the dissolution of the additions of clay minerals, which are different from clinoptilolite.

Sorption of divalent and trivalent cations from multicomponent solutions was studied. The modifying zeolite improves the sorption of metals, which are not related to d-elements. The attention was focused on Pb²⁺ ions since they are highly toxic (the maximal allowable concentration is 0.1 mg dm⁻³) [5]. As found, the removal degree of Pb²⁺ ions reaches 97%. The isotherm of Pb²⁺ sorption are fitted with Freundlich model. In addition to the lead extraction from aqueous solutions, the sorbent could be also recommended for water softening.

The composite based on natural zeolite containing hydrated iron oxide has been obtained. Its deposition in weakly alkaline media allows us to obtain nanosized particles of the modifier. As expected, it will accelerate the sorption of ionic species. It should be stressed that the modification improves the sorption of metals, which are not related to d-elements. The composite could be recommended for water softening and also for the removal of Pb²⁺ ions from aqueous solutions.

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Self-assembled FeOOH (OXY)Hydroxide on Colloidal Al:SrTiO₃ Perovskite as Solar Light-Driven Photocatalyst for Antibiotics Degradation

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Abstract ID #NEE- 0043

Tetracycline (TC), a broad-spectrum antibiotic, is one of the commonly environmental contaminants encountered in water due to its widespread use. Several strategies like biodegradation, physical absorption and advanced oxidation processes have been studied for removal and degradation of tetracycline. Due to their efficiency, advanced oxidation techniques like photocatalytic processes are considered promising and also environmentally sustainable strategy for the treatment of TC in wastewater [1]. In order to remove TC from aqueous solution, a visible-light photocatalyst based on SrTiO₃ nanoparticles [2] decorated with a double co-catalyst system consisting of Al₂O₃ and iron oxyhydroxide (δ-FeOOH) was developed and its photocatalytic performance was investigated. The self-assembled photocatalyst was characterized by X-ray diffraction, Scanning Electron Microscopy (SEM) and UV-Vis spectrometry. The photocatalytic performance of the material was evaluated by performing photocatalytic tests on different concentrations of tetracycline. The TC concentration at different irradiation times with visible light was monitored using off-line Reverse Phase High Performance Liquid Chromatography operated in isocratic conditions using a C18 based separation column. The performed photocatalytic experiments demonstrated that the tested material, Al: SrTiO₃@δ-FeOOH exhibit very good photocatalytic activity, over 90% of the tetracycline being degraded in 90 minutes.

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REFERENCES
The Role of Carbon Black Filler in Electrospun Composite Polymer Fibers for Enhancing their Electrical Conductivity and Mechanical Properties

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Abstract ID #NEE-0049

Electrospinning is an alternative way to fabricate conductive polymer fibers with adjustable mechanical properties and conductivity. Organic materials, primarily conjugated polymers, are unique for this purpose. However, due to their low solubility in solvents and low molecular weight, it is a challenging task to obtain a stable electrospinning process for intrinsically conductive polymers [1]. One of the solutions for this problem is to use the conductive filler in electrospinning non-conductive polymer solution to produce composite fibers. Here carbon-based materials such as graphene oxide, carbon nanotubes, and carbon black (CB) are great candidates as fillers and for increasing the electrical conductivity of polymer fibers [2] while providing additional mechanical resistance [3]. In this study, different non-conductive polymers were used for blend electrospinning with CB. We verified the effect of CB on electrospun fibers' and membranes' electrical conductivity and mechanical properties. The obtained results show the common strategies for incorporating CB in the electrospun fibers to produce high-performance membranes for smart materials and energy harvesting applications.

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REFERENCES

Technological Challenges in Electrospun Thermoelectric Polymer Fibers and Composite Materials for Energy Harvesting Applications

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Thermoelectric materials become more and more attractive in the extensive energy consumption needs. The demand of sustainable sources such as thermoelectric generators (TEG’s), and other devices allowing the conversion of heat energy into electrical power are extensively researched for energy harvesting applications [1, 2]. Due to many limitations of conventional ceramic-based thermoelectric materials (e.g. Bi$_2$Te$_3$, PbTe, CoSb$_3$) numerous development of the novel materials are directed towards flexible, light weight and low costs of polymers. One of the continuously progressing materials in electronics and nanoelectronics, biomedical devices and sensors are electrospun fibers. Electrospinning offers undoubtedly countless advantages in producing membranes, characterized with high surface area to volume ratio, with the scale up possibilities [3]. However, it is still challenging to manufacture thermoelectric electrospun fibers. Nevertheless, electrospun composite fibers with the additions of carbon- or ceramic-based fillers give wide perspective of combining thermal insulation properties of polymers and electric conductive properties, including polymer electrical conductors. Therefore, within this work the current achievements and future challenges in the field of electrospun thermoelectric fibers technology are provided. A variety of problems and current solutions are discussed, including materials, electrospun fiber’s role in thermoelectric power generation, concepts of design and fabrication or thermoelectric properties and characterization methods. This study indicates the wanted and necessary strategies to develop high performance thermoelectric membranes for energy harvesting applications.

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REFERENCES


Ceramic Materials in the Service of Nature: the Use of Al₂O₃ & TiO₂ in the Removal of the Organic Dyes from Wastewater

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One of the main reasons for the constantly increasing level of environmental pollution is the trouble with the utilization of synthetic organic dyes which come from the industry. Therefore, low-cost and effective methods of their removal from wastewater are sought [1]. The aim of this research was the evaluation of the photocatalytic activity of Al₂O₃/TiO₂ blends and the analysis of their physical properties. Blends of nanometric Al₂O₃ and TiO₂ powders in different mass ratios were prepared by the granulation process. The chemical composition of obtained blends was characterized by the X-ray powder diffraction method. Apparent density and specific surface area measurements were performed. Degradation of Eosin Y in an aqueous solution under visible light was conducted. UV-Vis spectroscopy was applied in order to observe the changes in the dye concentration. Color measurements of powders before and after the photodegradation process were carried out using a sphere spectrophotometer in the CIELab color space. The most effective in the removal of the Eosin Y process were the powders with 100 and 75% TiO₂ content. The photocatalytic abilities were confirmed for all of the tested samples. And so, it was proved that obtained powders can be applied successfully in the Eosin Y photodegradation. Moreover, based on the physical properties of Al₂O₃/TiO₂ blends it is expected they can be used for the formation of protective coatings by means of thermal spraying processes [2].

REFERENCES

Influence of Chemical Composition and Surface Topography of Nanostructured Epoxy Resin DER – 331 on Combined Biofilm Formation in Modelling of Biofouling

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In the context of greening science and technology, the need to develop safe composite nanomaterials to protect the surfaces of ships and structures is becoming increasingly important and is one of the main economic priorities of the European Green Deal. This article analyzes the results of research on composite material based on epoxy oligomer DER - 331 with biocidal fillers (nanosilver and oxytetracycline), which are recommended for protecting metal surfaces. The proposed two-stage approach in the study of protective composite coatings involves the study of the ecotoxicity of nanomaterials with different contents and combinations of fillers. The study of the ecotoxicity of metal samples with nanostructured epoxy coatings was conducted in vitro model systems using the indicator microorganism Bifidobacterium bifidum. Confirmation of the environmental safety of the nanocomposite determined the feasibility of conducting the second stage of research, which evaluated the effectiveness of composite surfaces for protection against biofouling. Estimating the dynamics of changes in the formation of a two-component biofilm on the composite surfaces of metal test plates using strains of Escherichia coli and Klebsiella pneumonia was the basis of studies in the second stage of research on the protective characteristics of epoxy resin DER - 331 with fillers. The formation of a two-component bacterial biofilm on the surfaces of experimental samples was studied in vitro model system. Considering the prolonged terms of biofilm formation under natural conditions, two reference time points for fixing the results (120 and 240 hours) were chosen to study the biofilm formation process. The obtained data show that the components of the composite surface of the test samples for 240 hours inhibit the formation of biofilm in the later stages. There is a significant (p≤0.05) decrease in the total volume of the formed combined biofilm in the test with the results for 120 hours of the experiment. The reduction in the total volume of the formed biofilm by 240 hours of the investigation may be due to the presence of fillers (nanosilver and/or oxytetracycline) and topographic features of the surface. The presence of a porous surface structure of samples based on epoxy resin DER-331 along with the biocidal properties of nanosilver and oxytetracycline fillers (q = 0.050 parts by weight and q = 0.075 parts by weight) changes the dynamics of biofilm formation, inhibiting its maturation. The combination of topographic features of the study samples and the chemical composition of nanostructured surfaces of the epoxy oligomer DER-331 works in favour of synergy in braking the formation of biofilms, which initiate the overall process of biofouling of surfaces.

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New Scintillation Materials Based on Hybrid BGO/LGSO: Pr and CsPbBr\textsubscript{3} Samples

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Abstract ID #NEE-0072

The search for new scintillation detectors for use in positron emission tomography is important for significantly improving medical diagnostics and the accuracy of high energy physics (CERN) experiments. It was shown that the detectors made of a crystalline substrate and a layer of material with fast luminescence allow combining the useful parameters of the applied starting materials (efficiency of absorption of ionizing radiation of the substrate, fast luminescence of a thin layer). Scintillators with a high effective atomic number, such as bismuth germanate Bi\textsubscript{4}Ge\textsubscript{3}O\textsubscript{12} (BGO) or lutetium-yttrium oxyorthosilicate doped with praseodymium (Lu\textsubscript{2}Y\textsubscript{2}SiO\textsubscript{5}:Pr (LYSO:Pr)) are commonly used as substrates for such detectors, and fast plastic, semiconductor, and other scintillators are used as the luminescent layer. Such systems have shown the possibility of obtaining a time separation of several tens of picoseconds.

In this work we considered new scintillation materials of the luminescent layer perovskite nanocrystals CsPbX\textsubscript{3}. Due to the quantum size effect, they have fast nanosecond luminescence. It is also possible to control their optical properties in a wide spectral range by replacing anions in the Cl/Br/I series, which leads to a change in the bandgap. Such properties of these nanoparticles allow us to consider them as scintillation materials. A colloidal solution of perovskite nanocrystals was prepared with LARP-technology. Optical and scintillation parameters of perovskite nanocrystals of polymethyl methacrylate (PMMA) film without substrate were defined. A complete characterization of two heterostructures based on two different heavy scintillators BGO and LGSO:Pr covered by a layer of colloidal perovskite solution was performed.

REFERENCES

Oxide Supported Anode-electrocatalysts for Proton Exchange Membrane (PEM) Based Water Electrolysis

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The Hydrogen Economy is a theoretical concept of a system in which hydrogen is the primary energy source and this concept is on track to come into reality. The main objective of a hydrogen economy is to produce hydrogen primarily from readily available energy sources to replace fossil fuels.

For the sustainable development of the hydrogen economy, green hydrogen production using water electrolysis technologies (WETs) is the only way forward. Among different WETs, PEM-WET is characterized by a fast response ramp-up and ramp-down capability and a wide dynamic operating range, making it ideal for generating hydrogen using excess renewable energy. PEM-WET is compact, low maintenance, and suitable for distributed hydrogen production applications. Therefore, to achieve the full potential of PEM-WET for large-scale hydrogen production, improvements in their cost/energy efficiencies are needed. The major reason for the high unit cost and/or lower efficiency of PEM-WET is due to the use of the high amount (loading) of noble metal catalysts and/or their inefficient utilization at the anode during the electrolysis. This high loading is required at the anode of the PEM water electrolyzer (PEMWE) to improve the kinetically sluggish oxygen-evolution-reaction (OER).

To date, IrO$_2$ has been recognized as the state-of-the-art OER catalyst, due to its stability and performance [1], in an acidic electrolysis atmosphere of PEMWE. As the use of IrO$_2$ is cost restrictive, to improve its cost-effectiveness and its better utilization, the IrO$_2$ is usually supported on an electrochemically stable, porous, electrically conducting, support with a high surface area. Typically, carbon is the most popular and probably most widely used ‘support’ material in this area of electrochemistry. However, during the operation of PEMWE, carbon support becomes oxidized to CO$_2$ (at a potential of > 1.4V), resulting in rapid degradation of PEMWE performance [2]. Therefore, there has been a great emphasis on developing alternative support materials to replace carbon. Among various candidates, metal–oxides are the preferred support material, as they have good corrosion resistance and exhibit strong interaction with the catalyst.

The majority of the studies on the oxide-supported catalyst suggest that the support oxides material remains inert for OER activity. However, if their incorporation results in de-agglomeration of noble metal oxide catalyst, interestingly, it results in superior performance (higher efficiency and longer life) [3, 4] with reduced catalyst loadings. The oxide support itself is not electrically conductive and therefore the use of a relatively high amount of IrO$_2$ (over 40wt.%) is required [5]. On the other hand, the use of electrically conducting and electrochemically stable oxides, such as titanium sub-oxide (Ti$_3$O$_7$), could mitigate the restriction of a relatively high amount of IrO$_2$ (> 40 wt. %) in oxide supported anode and its effectiveness will be presented at length.

REFERENCES

Enhancing the Capacitance of MXene Nanosheets via Intercalation of Water Soluble Ionic Liquids

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Room-temperature ionic liquids are rapidly emerging as solvents of choice owing to their intrinsic conductivity, low vapor pressure, and environmental friendliness. Their stability over a large potential window renders them useful as electrolytes for energy storage applications. The tunable cation-anion combination of ILs can be useful for intercalation in various materials such as rGO, MXenes, MOFs, etc. Additionally, given the current energy crisis, it is important to develop newer devices using sustainable materials for energy storage. MXenes have been shown to be promising electrode materials for supercapacitor applications due to their high conductivity and large surface area. Although ionic liquids have been used as electrolytes in MXene-based supercapacitors, they exhibit lower capacitance values compared to aqueous and organic electrolytes due to the stacking of MXene sheets leading to lower d-spacing values. [1] The use of small cations such as Na+, K+, Mg+, etc., has shown to enhance the capacitance of MXenes due to higher d-spacing.

In this work, we report the capacitative behavior of 2D MXenes intercalated with different imidazolium-based ionic liquids.[2] Owing to the negative charge on Ti₃C₂Tx sheets, we choose ILs with variable carbon chain length (EMIM+, BMIM+, and HMIM+) on the cationic part and a common anion (BF₄⁻). The water-soluble nature of the ILs makes them readily disperse in the aqueous MXene solutions. Additionally, the large size of the cations compared to the metal ions leads to an enhanced interlayer spacing of the MXene sheets. Aqueous Ti₃C₂Tx dispersions were stirred in the above-mentioned ILs for 24 hours to ensure proper intercalation. The composite materials were studied using various microscopic and spectroscopic techniques. A considerable shift in the 002 peak of Ti₃C₂Tx to a lower 2 theta value is observed in the PXRD data. The peak shift is higher for the IL with the longest carbon chain i.e. HMIM BF₄. Furthermore, FESEM images also show an expanded structure confirming the interlayer separation of the 2D sheets. Electrochemical studies were performed using conventional 1M H₂SO₄ electrolyte. The highest capacitance is observed in the case of BMIM BF₄ intercalated MXene (~283 F/g), followed by EMIM BF₄ (~234 F/g), and Ti₃C₂Tx (~212 F/g) at a current density of 1 mA/g. Interestingly, HMIM BF₄ intercalated MXenes exhibited the lowest capacitance, possibly due to the poor solubility of the IL in water. Furthermore, electrochemical studies in Ionic liquids also exhibit a similar trend in the capacitance values. This enhancement in the electrochemical performance further paves way for using MXenes and ionic liquids for energy storage applications.

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REFERENCES

Porous Nanocomposite Based on Natural Clay Minerals

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Nowadays, porous nanocomposites have a high potential for diverse practical applications (adsorbents, catalytic support and catalysts, sensors, and carriers). Special consideration is given to materials based on inorganic matrices. As for which, natural and synthetic layered aluminosilicates (montmorillonite, saponite, hectorite, laponite) are usually applied [1]. Because high cation exchange capacity (CEC) and delaminations in polar media, such as water, distinguish these silicates from other silicates. Furthermore, materials based on clay minerals are stable when used in aggressive environments and elevated temperatures. As a reason, finding new and enhanced current technologies for the synthesis of porous nanocomposites is a critical issue.

The natural montmorillonite (MMT) from the Cherkasy deposit (Ukraine) was the object of this study. For all experiments, we used the sodium form of MMT. One of the possible methods of controlling the porous structure is using surfactants as templates and organosilicon compounds for connecting two adjacent sheets [2]. In our research, hexadecyltrimethylammonium bromide (HDTMABr) was chosen as the template. That has a linear structure with 19 hydrocarbon radicals compensated by the Br- ion. It is important because the length of the CH₂- radical and the concentration of surfactant affect the form of future pores. Tetraethylorthosilicate (TEOS) was employed to prop up the increased space after the surfactant and additional silicon source. The experimental method involved gradually adding a sol-solution for intercalation to 1% of the clay suspension in various HDTMA /CEC mass ratios. After that, the samples were dried at 80 °C and calcined at 550 °C for 6 h.

Analytical research methods were used to study the obtained porous composites: X-ray powder diffraction, low-temperature N₂ adsorption-desorption method, FTIR spectroscopy, and thermogravimetric analysis.

The X-ray diffractograms and IR-spectra confirm the successful intercalation of HDTMA in the interlayer space of the MMT. Depending on the ratio of HDTMA/CEC changed the main characteristics of the porous structure of the samples. The obtained results indicate that the specific surface area increases with the amount of surfactant introduced by 1 CEC, the maximum SBET equal to 225 m²/g. The total pore volume and average pore radius also increase while the number of micropores decreases. At the same time, there is a wide distribution of mesopores by size.

An essential stage in developing porous nanocomposites based on clay minerals is to investigate the interaction of the original system's components to anticipate their structural properties. In future research, it is necessary to develop porous nanocomposites on various inorganic matrices similar to MMT and compare their properties.

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Electrical Properties, Photoresponse, and Structural Properties of CdZnTeSe Thick Polycrystalline Films

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Thick polycrystalline CdZnTeSe films were deposited by close-spaced vacuum sublimation method. The electrical properties, photoresponse, and structural properties were studied by electrical measurements, scanning electron microscopy, X-ray diffraction. Using the light excitation of the visible range the photoresponse of detector structures based on CdZnTeSe films was measured.

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Photocatalytic Degradation of Toxic Pollutants from Waste-Water by Thermally-Modified Graphitic Carbon Nitride

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Abstract ID #NEE-0131

Water pollution is one of the greatest concerns of the present world which needs immediate attention and strict regulatory surveillance to prevent its paramount adverse effects on the environment. Chemical pollutants like coloured dyes and heavy metals are discharged from countless industries like textiles, tanneries, and pharmaceuticals which contribute extensively to contaminating freshwater resources of this planet whereby causing deleterious effects on all living organisms including human beings. Graphitic carbon nitride (GCN), comprised of carbon and nitrogen, is a distinctive material that procured massive prominence in recent times owing to its prospective applications in numerous practical fields, including wastewater purification. Substantial porosity and surface area, non-toxic nature, low-cost and high-yield of production along with notable stability and durability are some of the remarkable features possessed by GCN which in turn make it a promising contestant for catalytic activities. The present work reports the synthesis of thermally modified GCN by a two-step thermal treatment procedure and its subsequent utilization in the photocatalytic reduction of toxic pollutants like Rhodamine B dye (RhB) and chromium ions (Cr$^{6+}$) from water environment. The as-synthesized exfoliated GCN (GCNX) was characterized by different techniques like XRD, FTIR, XPS, BET, DRS, PL and TEM to elucidate the phase formation, chemical structure, surface area, optical properties and morphology of the sample. GCNX was able to degrade RhB dye within 30 min of visible light irradiation in presence of H$_2$O$_2$ whereas the same sample could effectively reduce Cr$^{6+}$ to Cr$^{3+}$ within less than 2 hr. in presence of Formic acid (FA) and visible light source. Variations in different catalytic parameters were performed to study their effects on the degradation activity of GCNX. These include variation in catalyst amount, pH, initial RhB or Cr$^{6+}$ concentration, variation in H$_2$O$_2$ or FA concentration etc. The results showed that improved degradation rates could be achieved by varying these different catalytic parameters. Moreover, the effect of various salts present in water was also analyzed. The GCNX catalyst was reused for several catalytic cycles to study the stability of the catalyst. Thus the as-synthesized non-toxic low-cost stable and efficient catalyst material can be successfully employed in waste-water purification in future.

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Effect of Using TiO$_2$ Nanotubes as a Substrate on the Properties of ZnIn$_2$S$_4$ Layers

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Abstract ID #NEE- 0138

TiO$_2$ is a compound of great importance due to its unique catalytic properties and characteristic semiconducting properties. It is also a chemically stable, non-toxic and biocompatible material. The preparation of nanotubes of this compound allows mainly to expand the surface of the material, but also to control its chemical and electrochemical properties by changing the synthesis parameters [1]. TiO$_2$ nanotubes (TiO$_2$NT) layers can also be substrates for the deposition of active materials to obtain composite photoelectrodes.

ZnIn$_2$S$_4$, as a representative of the group of ternary sulfides, is a promising material with photocatalytic properties towards water splitting due to its suitable arrangement of energy bands, sufficient ability to absorb visible light, and low environmental toxicity [2]. However, due to the strong recombination of charge carriers and the slow dynamics of surface oxygen evolution reactions, the performance of ZnIn$_2$S$_4$ as a photoanode is still not satisfactory. So far, many options have been described to enhance the performance of ZnIn$_2$S$_4$ as a photoanode, such as morphology modifications or deposition of other catalysts [3], [4]. Most works on the use of ZnIn$_2$S$_4$ as photoanodes describe layers of this compound deposited on FTO [5].

This study presents a comparison of the properties of ZnIn$_2$S$_4$ layers obtained on TiO$_2$ nanotubes with those obtained on the most commonly used substrate for photoanode materials – FTO glass. ZnIn$_2$S$_4$ layers on FTO and TiO$_2$ nanotubes were obtained using a hydrothermal process previously described in the literature [5]. The resulting materials were then annealed at different temperatures. Electrochemical and photoelectrochemical studies were performed in a three-electrode system under simulated solar light illumination. The values of photocurrents generated by the tested photoanodes were determined using linear sweep voltammetry and chronoamperometry. The most suitable annealing temperatures for the materials were different for the two substrates. The most significant differences between the obtained photoanodes involve the generated photocurrents and their stability. FTO/ZnIn$_2$S$_4$ photoanodes generated higher photocurrents of water oxidation during short-term illumination than TiO$_2$NT/ZnIn$_2$S$_4$. However, longer illumination under potentiostatic conditions (> 200 s), showed much higher stability of photocurrents generated by TiO$_2$NT-based photoanodes than those obtained using FTO.

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Selected Aspects of Oxygen Speciation in Nanopowders of Semiconductor Kesterite Cu$_2$ZnSnS$_4$ Prepared by Mechanochemical Synthesis From Metal Sulfide Precursor System

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Presence of various oxygen contaminations will impact the semiconductor properties of quaternary sulfide Cu$_2$ZnSnS$_4$ – kesterite, which determine its future use as an active semiconductor layer in photovoltaic cells. Oxygen in kesterite can be present on particle surfaces mostly in sulfate groups and as a substitute for some sulfur centers in the crystal structure. It can originate from adventitious surface oxidation of precursors and of the product itself whereas some oxygen contents can also be linked to adsorption of water vapor and oxygen from ambient air upon handling/storage. This work presents the results of determination of the total oxygen and some specific oxygen forms contents in kesterite nanopowders as well as their influence on the bandgap energy.

Kesterite was prepared by a two-step synthesis route from the original precursor system of metal sulfides and sulfur [1]. In the first step, a suitable mixture of the sulfides Cu$_2$S, ZnS, SnS and sulfur S was mechanochemically reacted in a high energy ball mill for 20 h at 900 rpm with xylene as a dispersion liquid. The second step included annealing of the dried-up raw solid at 500 and 550 °C for 6 h under an argon flow. The precursors and resulting materials were examined by powder XRD, UV-Vis spectroscopy, FT-IR spectroscopy, and oxygen content analysis (LECO ONH 836).

The raw material after milling had a cubic sphalerite-type structure (pre-kesterite) showing no semiconducting properties and surprisingly high O-content of the order of a few weight percent. The annealing caused transformation to the tetragonal kesterite materials that had the anticipated bandgaps and much lower O-contents. The FT-IR spectra displayed marked differences among the oxygen-related bonds detected in the pre-kesterite and kesterite nanopowders.

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Nanocomposites Based on Electrospun Polyamide Nanofibers Modified by Metal Oxide Manowires – MXene Towards Photocatalytic Applications

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Abstract ID #NEE-0153

Due to the high surface-to-volume ratio and good physical properties of polymeric nanofibers, they are widely used in various applications such as micro-filtration, protective clothing, photocatalysis and sensor. There are various techniques to produce polymeric nanofibers, among them, electrospinning is regarded as the most versatile and tailorable technique because it offers the ability to produce ultrathin nanofibers with diameters ranging from tens of micrometers to several nanometers.

Polyamide (PA) is an important biocompatible polymer with very good mechanical properties used for e.g. the preparation of bone scaffolds or for antimicrobial material. In the proposed research, the nanocomposites based on electrospun PA nanofibers have been used for photocatalytic applications. In order to achieve the photocactivity, the well-known transition metal oxide photocatalyst have been combined with the polymer. Transition metal oxides and their application in the development of diverse photocatalytic nanomaterials are a topic of great interest over the years. Different combinations of transition metal oxides such as TiO$_2$, ZnO, WO$_3$, or Fe$_2$O$_3$ were successfully employed in the fabrication of complex nanocomposites for water-splitting, dyes photodegradation via changing of its optical and electrochemical properties. A variety of porous, 1D, 2D and hierarchical nanostructures were reported in a vast amount of research, but still being a promising avenue for further development and investigation. The main challenge in such endeavors is the scalability and relative simplicity of the fabrication process of the aforementioned materials.

One of the well-developed and effective methods in this regard is electrospinning. It is a low-cost and relatively simple method for the production of polymer nanofibers in quantities. An introduction of different nanoparticles or nanowires in the initial polymer solution allows for their containment in the polymer fiber and after subsequent calcination (carbonization) allows the fabrication of nanofibers of desired composition. This approach can be applied to the fabrication of heterojunctions and various nanocomposites. And the resulted nanocomposite material can be used for further engineering of a photocatalyst. Besides, the electrochemical performance of metal oxides can be improved by their modification of MXenes, a new class of 2D carbide materials.

Here, we report a fabrication process, structural and optical properties of PA nanofibers with introduced TiO$_2$ and WO$_3$ nanowires modified by MXene nanoflakes suitable for efficient employment in photocatalytic applications.

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The Effect of Expanded Graphite on the Caloric Properties of Paraffin Wax

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Abstract ID #NEE-0170

Expanded graphite (EG) is a promising component to improve the thermophysical properties of paraffin wax (PW) for its use as a phase change material (PCM) for thermal energy storage (TES) systems. The selection of the rational mass fraction of EG in PW will help enhance the thermal conductivity and caloric properties of composite PCM that will contribute to improving the efficiency of the whole TES system.

The objects of the experimental study were: industrial PW with a melting point of about 50 °C, PW containing 0.032, 0.0362, and 0.0399 g·g⁻¹ of EG. The procedures of previously vacuuming the molted PW and EG with further vacuum impregnation of EG by PW were utilized during composite PCM preparation. Using the proposed preparation technique contributes to enhancing the composite PCM quality by nearly full removal of air from samples. The selected narrow range of the fraction of EG in PW was because of the following. Using an EG fraction less than 0.032 g·g⁻¹ did not allow for obtaining the stable composite PCM (without separating the portion of pure PW from the composite PCM). Concurrently, using an EG fraction greater than 0.0399 g·g⁻¹ will contribute to the deterioration of the caloric properties of the composite PCM. The measurement of the total enthalpy of phase transition and specific isobaric heat capacity of the composite PCM samples was performed by monotonic heating in the calorimeter of variable temperature. As a result, the time dependences of the effective isobaric specific heat capacity during heating and cooling for all samples in the temperature range of 25...70 °C were obtained.

It was observed that the presence of EG in PW contributes to a slight shift in the temperatures of the start and finish of the phase transition. Furthermore, it was shown that the presence of EG in PW contributes to enhancing the total enthalpy of phase transition up to 24 % (depending on EG mass fraction), which is promising for application in TES systems. The obtained results can be explained by the opposite influence of the two factors. The first is that the total enthalpy decreases in the presence of the EG, which does not participate in a phase transition. The second is that the total enthalpy increases by the structural changes in the PW caused by the formation of the ordered interface structure from PW molecules on the EG surfaces and PW crystallization in the limited volume of EG pores. The contribution of the second factor to the phase transition total enthalpy change is predominant for the analyzed EG mass fraction in PW. It was also recorded that EG presence contributed to increasing the effective specific heat capacity of PW in a temperature range below PW melting point, which is additional confirmation of the presence of structural changes in the PW containing EG. Further studies of the caloric properties of PW containing EG with a mass fraction of more than 0.04 g·g⁻¹ are necessary to explain the obtained effects.

ACKNOWLEDGMENTS

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Complex Experimental Investigation of the Effect of Fullerene C₆₀ on the Thermophysical Properties of O-xylene

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Abstract ID #NEE- 0197

The paper summarizes the results of a comprehensive experimental study of the effect of fullerene C₆₀ nanoparticles on the thermophysical properties of o-xylene [1–3]. It is shown that all investigated thermophysical properties (density, viscosity, saturated vapor pressure) in the range of fullerene concentrations of 0-0.2 wt.% behave non monotonically with an extremum near (0.05±0.01) wt.%. This specificity is associated with structural changes in the liquid phase at low concentrations of fullerene. The study was performed on identical objects, so the results and conclusions can be considered objective. Investigation of nanofluids has a number of specific problems [4]; however, the practical interest in their application is so high that thousands of different combinations of base fluids and nanoparticles added to them have already been studied. Nevertheless, there are still no universal laws and models for describing the physical properties of nanofluids in a wide range of state parameters. Every new system requires a large-scale experimental study because its properties cannot be found in any database.

In the present study, trying to reduce the number of factors that need to be considered when studying nanofluids, we have applied ideas of the fluctuation theory of liquids [5] to our model nanofluid – solutions of nanosized fullerene C₆₀ in o-xylene. This theory allows removing the artificial barrier between the regular and singular regions of the phase diagram, giving a decisive role in changing the thermodynamic parameters to the fluctuations. It was shown that the influence of a number of factors on the thermophysical properties of nanofluids can be reduced to a single-factor analysis, taking as a generalizing factor the temperature and concentration behavior of the density fluctuations. In contrast to the existing view that the thermodynamic properties of nanofluids depend only on the state parameters, we have established the need to take into account the structural changes in the base fluid associated with the addition of nanoparticles. This approach allows performing the express analysis of probable structural changes in poorly studied nanofluids in a wide range of state parameters using a minimum of experimental data, which is of great practical importance.

In addition, it is proposed to evaluate the thermodynamic similarity of liquid systems by a similar behavior of the temperature dependences of their density fluctuations, the specific heat of evaporation, or isothermal compressibility. For example, for the studied system fullerene C₆₀/o-xylene, these curves showed an equidistant character, which, in the author’s opinion, indicates the thermodynamic similarity of solutions with the base fluid. This significantly expands the possibilities of methods for predicting the properties of liquids usually based on traditional criteria of thermodynamic similarity (Pitzer, Riedel, Morachevsky, critical compressibility, etc.).

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Conference Track: “Nanomaterials for Energy & Environment”
Energy Harvesting by Mini-Converters Based on Nanostructured Silicon

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Abstract ID #NEE-0200

Modern wireless sensor networks consist of many sensor devices to collect and transmit their data. Various types of sensors (ultrasonic, gas, temperature, and motion), with difficult access to the power source, are equipped with batteries as a wireless power source. However, these batteries have a limited life span and require periodic replacement. Thus, batteries cannot be suitable for biomedical devices, environmental or industrial monitoring, and the military sphere. Therefore, as an alternative to an electrochemical battery, environmental energy is preferable for such electronic devices with a limited lifetime. Micro-power energy harvesters can significantly extend battery life where battery replacement is difficult or impossible. Among various types of environmental energy, such as motion, vibration or sound, thermal or wind, solar has great potential for energy harvesting due to its abundance. It is a virtually inexhaustible energy source with little or no negative impact on the environment. Electricity is generated by converting solar radiation (indoors and outdoors) into direct current electricity using semiconductors that exhibit a photovoltaic effect.

This paper presents an effective and inexpensive method of texturing the silicon surface to obtain nanostructured silicon layers with different morphology and distribution of chemical elements on the surface of the substrate. The presented method of forming nanostructured silicon films by chemical etching demonstrated good reproducibility of the results. Single-crystal silicon wafers for the production of solar cells were the subject of experiments. The plates were boron-doped and had p-type conduction. The substrates had a resistivity of 1 Ohm / cm², (100) crystallographic orientation, and a thickness of 350 μm. The study of current-voltage characteristics of nanostructured silicon was performed in the visible range of the spectrum. The structures of monocrystalline p-type silicon – nanostructured silicon – aluminum, created based on the obtained films of nanostructured silicon, showed a photoelectric effect. Among the tested layouts, the best results were obtained for a structure with a nanostructured silicon film thickness of 35 nm. The resulting photocell had an area of 0.5 cm². In this case, the resulting structures show a photoelectric effect (0.2 V, 90 μA under load) under indoor illumination (electric and/or solar). The resulting mini power converters based on a nanostructured silicon film can be combined in panels to obtain the required voltage or current. Created mini power converters based on a nanostructured silicon film, and their panels, can be integrated into electronic circuits and ready-made chips for various purposes with low power consumption. The latter opens up the possibility of using nanostructured silicon in photonics, photoelectric devices, biophotonics, and biosensors.
Photocatalytic Activity and Synthesis of Silver Nanoparticles in the Presence of β-cyclodextrin and Titanium Dioxide

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Abstract ID #NEE-0209

I In this work, the samples contained TiO2 and silver nanoparticles (1%) and were synthesized by various techniques for study the photodegradation of methyl orange. For comparison purposes, we used the neat TiO2 (Aldrich), TiO2/Ag obtained by mechanical mixing of titanium dioxide with silver nanoparticles (Aldrich), and a sample obtained by the reduction of silver ions using UV radiation. The reduction of silver ions was carried out in a suspension of TiO2 with NaOH or NaBH4 in the presence of β-cyclodextrin (β-CD) at a temperature of 85°C. It was found that the reduction of Ag+ ions in the solution using NaOH in the presence of β-CD was more efficient than without it. In the UV spectrum, the surface plasmon resonance (SPR) band of silver nanoparticles was significantly more intense after during 6 h heating, although its position was slightly shifted to the long-wavelength range (412 nm vs 420 nm). The SPR band was observed at 398 nm, and it was significantly narrower than without the use of β-CD upon reduction in the NaBH4/β-CD system. The photodestruction was carried out in a quartz tube with an aqueous solution of methyl orange (MO) and 40 mg of the sample. The final TiO2 concentration was 1 g/L, MO were 15 and 30 mg/L. Distilled (pH 5.3-5.5), artesian (pH 7.15-7.30) and river water (pH 6.98) were used for this research. The resulting mixture was irradiated by three UV lamps (8 W) with a wavelength of 365 nm and 254 nm. It was found that in a weakly alkaline medium, the photodegradation of MO for the neat TiO2 was slowed down. Comparative analysis of the effectiveness of the studied samples was performed using UV spectroscopy. In the distilled water at an initial MO concentration of 15 mg/L for 20 min of irradiation when using TiO2/Ag (CD-NaOH) as a catalyst, the solution was completely decolorized, while for neat TiO2 only 39.3% MO decomposed after 30 min. The sample TiO2/Ag(CD-NaOH) turned out to be the most effective at a concentration of 30 mg/L, because absorption bands in the UV spectrum were not observed already after 60 mins of irradiation. When using a TiO2/Ag(UV), after 60 mins of irradiation, only a fairly intense absorption band at about 200 nm was observed, as for other compounds except the samples obtained with β-CD. In the artesian water for the neat TiO2, photodegradation proceeded rather slowly. For 100 min of irradiation, 48% of the initial MO concentration remained in the system, while when using the sample TiO2/Ag(CD-NaOH), a full destruction occurred during at the same time. It should also be noted that for all the studied samples in the river water up to 60–80 min, photodegradation was slower than in the artesian water. The obtained results showed that the use of β-cyclodextrin in the synthesis of photocatalysts based on silver and titanium dioxide is an effective way to improve the photocatalytic properties.

REFERENCES
Polystyrene/BiFeO$_3$ Thin Films for Vibrating Sensing and Energy Harvesting

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Abstract ID #NEE- 0228

The application of strain sensors allows the monitoring of the behavior of load-bearing elements in automotive, aviation, aerospace, and construction [1–4]. In structural health monitoring (SHM), commonly used solutions are optical sensors [3,4], vibrating wire [3], piezoresistive [2-3] and piezoelectric sensors [5], which are mounted to the construction or integrated into the composite structure. The main purpose of SHM’s application is to ensure the safety of the structure by the means of registering and identifying possible dangerous overloads, such as high pressure or vibrations, which are extremely dangerous for load-bearing elements.

One of the factors that can’t be totally eliminated is vibrations, especially in automotive or aviation [3-5]. However, proper monitoring of its level allows for preventing major damage, while vibration with low intensity can be used for energy harvesting. Materials that can convert vibrations or strain into electricity are commonly known as piezoelectric, in which the perovskites structures should be mentioned.

The aim of this study was to investigate the effect of BiFeO$_3$ (BFO) nanoparticles' weight amount (1-20%) on the properties of polystyrene/BiFeO$_3$ thin films. BFO nanoparticles were fabricated using the facile reverse co-precipitation method, followed by annealing and ultrasonic dispersion in ethyl acetate, which was used as a solvent for polystyrene granules. Obtained mixtures were solution-casted on glass plates, cut into proper shape and gold electrodes were sputtered on both sides. Prepared thin films were characterized by means of filler dispersion (SEM), structure (XRD, DSC) and piezoelectric response for vibrations with different frequencies. The main advantage of proposed sensor is the fact that can be easily mounted on different surfaces and used for vibration sensing and energy harvesting.

REFERENCES

Nanoengineered Photocatalysts for Selective Reduction of CO₂

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Abstract ID #NEE- 0252

Photocatalysis, in terms of green chemistry, is one of the promising methods for the performance of tough reactions, as it is driven by light. P25 (TiO₂ anatase-rutile photocatalytic standard) is a highly active material, efficiently photocatalysing chemical transformations [1]. However, in terms of CO₂ reduction, P25 is not effective enough. Modifications (e.g., structure, surface) or combination with other semiconductors (e.g., formation of heterojunctions, Z-scheme systems), can be used to enhance the photoactivity of the materials and control the selectivity of the reaction [2].

In this work, we designed an advanced photocatalytic system for CO₂ reduction. P25 was combined with a nanocomposite, which is built of magnetite (Fe₃O₄) doped with Sn (micro octahedra) modified with cassiterite (SnO₂) nanoparticles doped with Fe (obtained in one synthesis route). The structure of obtained nanocomposite was established using SEM, TEM microscopies, as well as XRD, XPS and Mössbauer spectroscopies. The formation of a junction was analysed using a Kelvin probe. The photoactivity was examined in the gas phase reaction, using gas chromatography. It was found, that synthesized composites enable a selective CO₂ reduction to CO.

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Tin and Iron Oxides as Photocatalysts for CO$_2$ Reduction

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Nowadays many people consider the rising environmental and energy concerns and seek to alleviate them with photocatalysts capable of reducing CO$_2$, which is a greenhouse gas, into value added chemicals or so called solar fuels using the supply of energy from our Sun. However, many well-known photocatalytic materials exhibit too wide band gaps limiting the absorption spectrum to ultraviolet range which covers only a small fraction of solar radiation. Some other materials suffer from too weak reductive properties due to insufficiently low potential of the conduction band edge. These shortcomings can be alleviated by combining two materials, one being an oxidative photocatalyst and the other – a reductive photocatalyst forming the so called Z-scheme. In such a system at the expense of absorption of two photons of lower energy (potentially visible range which is the main component of solar spectrum) electrons of energy high enough to reduce CO$_2$ can be obtained along with a hole which can oxidize a hole scavenger (for example water) to return the system to ground state. Such a system could be realized with for example the Tin and Iron Oxide (SFO) which is a semiconductor offering a high conduction band level and an oxidation photocatalyst. This presentation deals with a photocatalytic CO$_2$ reduction at SFO, both alone and in combination with other materials, and the synthesis of SFO.

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Novel Nancomposite Polymer Granules for Selective Removal of Cesium Radionuclides

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Abstract ID #NEE- 0259

The operation of nuclear power plants and nuclear facilities is accompanied by the formation of large volumes of liquid radioactive waste (LRW) and an increase in the risk of radionuclide release to the environment resulting from nuclear accidents (Chornobyl and Fukushima, for example). Low- and intermediate-level LRW poses a significant environmental hazard because of its large volume and high total activity. The primary purpose of LRW management is to reduce radiation activity and volume. Among the conventional techniques developed for wastewater treatment, the adsorption process is mostly used for the selective removal of various soluble radionuclides. However, several specific requirements for adsorbents used in nuclear technologies have been formulated, including high selectivity toward the targeted radionuclides, fast interfacial reactions, good physicochemical as well as mechanical and radiation stability, and low cost. These criteria are met by some inorganic synthetic nanomaterials.

Nanomaterials, due to the “nano-size effect” (large specific surface area, fast reaction rate, higher adsorption capacity, etc.), have become the next generation of adsorption materials for radioactive wastewater treatment. However, nanoadsorbents have not found a wide application owing to their quick agglomeration, compaction, loss of chemical activity, and difficulties in the separation of the spent adsorbent from the purified solution. The last achievements in nanotechnology allow overcoming these technical drawbacks through the synthesis of nanocomposite adsorbents.

Here we report the synthesis of a novel nanocomposite adsorbent based on macroporous polymer granules for selective removal of $^{137}$Cs radionuclides. The insoluble metal hexacyanoferrates (HCFs) are considered highly selective inorganic adsorbents for $^{137}$Cs over a wide pH range, even in the presence of high salt content. However, low hydromechanical stability and nanoscale grains of the as-synthesized HFCs caused some limitations in their practical application. A novel nanocomposite adsorbent based on commercially available macroporous polystyrene resin with sulfonic acid groups was successfully prepared by in situ formation of potassium copper hexacyanoferrate (KCu HCF) phase inside the polymer granules. Results of X-ray diffraction and scanning electron microscopy studies confirm the formation of the KCu HCF phase in the form of rounded nanoscale aggregates.

The efficiency of the synthesized nanocomposite adsorbent for the removal of cesium ions was evaluated under various experimental conditions. It was demonstrated a fast adsorption rate, high adsorption capacity over a wide pH range, and selectivity in Cs ion removal from model solutions with high content of competing Na and K ions. The synthesized nanocomposite adsorbent could find a large-scale application in the treatment of low-level LRW because of its high selectivity to Cs ions, simplicity, and low fabrication cost.
Synthesis and Application of Nanocellulose from Non-wood Plant Raw Materials

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Abstract ID #NEE- 0271

One of the urgent problems of humanity is the protection of the environment from plastics and polymers obtained from exhaustible natural resources. Today's problems require solutions using environmentally friendly products from renewable sources, in particular from plant materials, as an alternative to products from oil, gas, and coal. Such alternative products include nanocellulose, a new class of nanomaterials with unique properties.

Nanocellulose is a biodegradable material with high mechanical strength, stronger than steel, high transparency and chemical resistance, lightweight and low coefficient of thermal expansion, large specific surface area, and low cost. Therefore, nanocellulose is widely used in industry in the production of biopolymers and biocomposites, packaging and flexible, pharmaceutical science and medical applications, as well as hygiene and sanitation products. It is used to increase the mechanical strength and improve the barrier properties of paper and cardboard, polymer and cement composites, electric batteries, and sorbents.

An experimental study of the synthesis of nanocellulose from organosolv pulp (OP) from non-wood plant raw materials instead of wood, which corresponds to the strategy of sustainable development. The OP was obtained from renewable plant materials (wheat straw, reeds, flax, hemp, kenaf, miscanthus) by using the environmentally friendly organosolv method of delignification by extraction with NaOH solution and cooking using a mixture of acetic acid and hydrogen peroxide.

A stable, transparent nanocellulose gel was extracted from OP by three methods: 1) hydrolysis of OP with sulfuric acid solutions; 2) oxidation of the OP in the environment of 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) and 3) extraction of OP by deep eutectic solutions. For all three methods, the characteristics of nanocellulose were determined and compared depending on different values of technological parameters: reagent concentration, temperature, and duration of nanocellulose production processes. Morphological (SEM), structural (FTIR and XRD), and thermal characterization (TGA) of non-wood plant raw materials, OP and nanocellulose were carried out. Topography and nanoscale features of the samples were studied by AFM and TEM methods.

The values of particle sizes of nanocellulose and their mechanical properties (density, tensile strength) and transparency were established according to ISO standards. The properties of nanocellulose obtained by different methods from different representatives of plant raw materials are compared.

The possibility of applying nanocellulose in the composition of composite materials – electronic devices, epoxy resin, paper, and cardboard are analyzed. It is shown that the use of nanocellulose in the composition of composite materials allows obtaining products that meet the requirements of standards and replace environmentally harmful synthetic polymers from exhaustible energy sources - oil, gas, and coal.
MnO$_2$/TiO$_2$ Nanopowders-Assisted Photocatalytic Degradation of Low-Density Polyethylene Films

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Abstract ID #NEE- 0273

Nanomaterials of anatase TiO$_2$ (I, supplied by the Institute for Problem of Material Science of National Academy of Science of Ukraine (IPMS NASU) [1]), and ramsdellite phase MnO$_2$ (II, supplied by Prydniprovsky Chemical Plant, Kamyanske, Ukraine) were investigated separately and in the mixture for photocatalytic degradation of low-density polyethylene (LDPE) films. The size of shapeless anatase crystallites is ~10 nm and needle-like aggregated along the direction of growth crystallites of II have 20–30 nm thickness.

In this study, LDPE films were prepared by using the casting method reported in the literature [2] with some modifications. Briefly, paraxylene was as a solvent, and an ultrasonic stirring was applied to evenly distribute the inorganic catalyst in LDPE. The photocatalyst content was 1wt %: (I, II, and their mixture III in 1:1 ratio by wt.%). Polyethylene degradation tests were carried out for 90 hours inside a photoreactor with UV-irradiation (OUFK – 01 lamp, Ukraine). As shown in this study, I and II as individual additives were less effective comparing to the 1:1 mixture (14.6%, 6.55%, and 21.29%, respectively).

The composite LDPE films were characterized using the mass loss of photocatalytic degradation, TG, DTG measurements. The TGA device was Thermogravimetric Analyzer Discovery TGA550. The degradation of polyethylene film with composite III becomes visible at the lowest temperature (above 120 °C). The latter fact together with the synergistic effect of mass loss for LDPE degradation with nanopowder mixture III could be a response of the coupling effect between I and II semiconductors. The excitation of electrons to the conductivity band takes place at a lower temperature due to the narrower band gap of the catalyst. In turn, degradation starts at a lower temperature.

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Transformation of Nanopores in the MgO-Al₂O₃ Ceramics under Influence of Water

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Abstract ID #NEE- 0293

Humidity-sensitive elements based on nanostructured spinel MgO-Al₂O₃ ceramics are actively used in sensor electronics due to their ease of production, flexibility and stability of performance [1]. However, to obtain a material with predetermined properties, it is necessary to optimize the technological conditions for obtaining the structure of the main components (grains, grain boundaries, pores), which would maximize the adsorption and desorption of water and be resistant to other external factors [2].

The goal of this work is investigation of the evolution of extended defects as well as nanopores in the MgO-Al₂O₃ ceramics prepared at 1300 °C for 2 h at influence of water and microstructural properties and phase composition of ceramics.

Extended free-volume defects and evolution of nanopores at adsorption were investigated by PALS method using an ORTEC spectrometer. The researches were made for the initials samples of ceramics and after placing the samples in water for 12 h. Due to the details of the experiment, the obtained PALS spectra were analyzed by the LT computer program at decomposition into three components.

It is shown that microstructure, phase composition, features of pore size distribution of nanoporous MgO-Al₂O₃ ceramics prepared at 1300 °C for 2 h – humidity-sensitive material for active elements of sensor electronics were studied. It is shown that studied ceramics is described by developed structure of grains, grain boundaries with extracted edition phase and pores with different shapes and sizes. The investigated ceramics are two-phase, contains main phase of spinel and addition MgO phase. The porous structure of ceramics is described by the trimodal pore size distribution. In the study by PALS method it was shown that the presence of water in ceramics leads to the increase of positron trapping rate in defects, their slight expansion. The size of the nanopores was estimated by the lifetime of the third component according to the Tao-Eldrup model. It was shown that the adsorption of the water by ceramics leads to the fragmentation of free volume in nanopores. The value of lifetime of the third component off 1.88 ns in water-immersed ceramics also indicates the o-Ps decay in water.

REFERENCES

Direct-Indirect Graphene Fabrication of Cu-Based Solar Cells Contacts

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Abstract ID #NEE-0303

Cu-based thin-film metal contacts are considered to be a promising alternative to replace the Ag paste electrodes currently used in solar cells (SC), as they can significantly reduce manufacturing costs of photovoltaic devices. However, direct replacement of Ag by Cu is currently highly problematic due to fundamental limitations observed on Cu/Si contact interfaces and the propensity of Cu to oxidize. Thus, the idea of creating thin-film multilayer contact structures where the Cu layer is used together with buffer and coating layers that are made of various metals that do not have high conductivity but can protect the integrity of the Cu conductive layer during SC operation [1].

The use of Ni as a buffer layer can minimize possible problems of the Cu/Si couple without greatly compromising contact resistance required to ensure high performance of the device. Recently, it has been shown that the introduction of graphene mono/bilayers between the Cu and Ni can be useful due to possible increases in thermal conductivity [1] and mechanical properties [2] of the layered system. Though, fabrication of graphene on thin-film (~ 300 nm) metal substrates is still a big challenge [3]. Therefore, the present study focused on two different approaches: (a) direct, using of thermal solar chemical vapor deposition (TSCVD) on Ni and (b) indirect, involving the graphene TSCVD synthesis on a bulk polycrystalline Cu substrate followed by its transfer to the Ni base. Both alternatives were used to deposit graphene on 25-nm-thick Ni film prepared by magnetron sputtering on single-crystal Si.

SEM imaging of the surface of directly synthesized graphene showed island-type structure formation resulting of Ni agglomeration of at high temperature. AES depth profiling indicates the full intermixing of Ni with Si and silicide formation with close to equiatomic composition. Monosilicide NiSi presence has been verified by XRD and Raman spectroscopy. It follows from AES data that up to 60 at.% carbon is present on the Ni surface. The Raman spectra indicate that graphene is not entirely covering the Ni surface, while the carbon-containing areas on the surface likely consist of several layers of graphene. Even though the NiSi formation is desirable for contacts, the elevated temperature severely damaged the surface structure. The indirect graphene synthesis revealed better Ni surface structure; presence of up to 80 at.% of C on the Ni; and higher quality of graphene layer confirmed by Raman data (before transfer (on Cu): ID/IG~ 0.1, after transfer (on Ni): ID/IG~ 0.74). Transferring graphene from the Cu substrate to the Ni base did not cause any intermixing of Ni with Si and therefore no silicide formation. However, the use of the indirect approach is accompanied with a presence of Cl contaminants on the Ni surface, a residual reagent remained after the chemical reaction of graphene wet transfer from Cu. Overall, indirect approach led to higher graphene quality.

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Conference Track: “Nanomaterials for Energy & Environment”
Thickness Dependence of the Kinetic Parameters in CdTe and PbTe Thin Films

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Abstract ID #NEE- 0313

In contrast to single crystals, thin films have a significant surface-to-volume ratio. In some cases, the film thickness is the parameter that determines the transport properties and the dominant mechanisms of charge carrier scattering. It is known that, in the region of small thicknesses, the mechanisms of scattering in films differ significantly from those in bulk samples. In particular, it is necessary to consider scattering at interphase and grain boundaries, misfit dislocations, and other growth defects [1, 2]. Furthermore, the localization of current carriers on surface states and their capture by dangling bonds within crystallites lead to the formation of space charge regions near them, and the concentration and mobility of current carriers in which can differ significantly from the corresponding parameters in bulk. The degree of influence of near-surface regions on the properties of films depends on their thickness, structure, doping level, and temperature [3, 4].

In this work, we studied the features of the behavior of the resistivity and mobility of carriers as a function of the thickness of CdTe and PbTe films deposited on glass substrates. The glass substrates were thoroughly cleaned using water, NaOH, distilled water, and successive isopropyl alcohol. During deposition, the temperature of the substrates was at room temperature. The compensation method was used to measure the electrical parameters of the films in constant electric and magnetic fields. The measurement was carried out on separate films of different thicknesses. The current through the samples was about ≈100 μA. A magnetic field was directed perpendicular to the film surface at induction of 2 T. The measured sample had two current and four Hall contacts. Silver films were used as ohmic contacts. The films had a polycrystalline structure with crystallite sizes of 0.01–0.12 μm.

As a result of the studies, the dependence of the resistivity and mobility of current carriers of CdTe and PbTe films on the thickness was obtained.

It should be noted that the studied films are characterized by a size effect in the electrical resistance, i.e., it grows with decreasing thickness (increase in 1/d). In particular, when the film thickness changes from 0.3 to 0.05 μm, the mobility decreases by almost two orders of magnitude. The latter indicates that the “film–substrate” and “film–free surface” interfaces and intergranular boundaries affect the transfer phenomena associated with the value of the mean free path of charge carriers. One can see the observed increase in mobility with film thickness, which was confirmed experimentally and associated with an increase in the size of crystallites in films.

REFERENCES
Fabrication of Stable and Efficient Metal-Organic Frameworks Doped Triple Cation Perovskite Solar Cell

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Abstract ID #NEE- 0315

Metal halide perovskites are used for various energy devices due to their excellent properties like tunable bandwidth, ambipolar semiconducting behavior, superior electrical conductivity, etc. However, several challenges in front of them like propensity towards degradation in the presence of moisture, UV radiations, etc.

In this study, we investigated the role of the metal-organic frameworks (MOFs) in the Triple cation perovskite (TCP) solution, its effects on their crystal growth, film formation, and photovoltaic performance. By employing Zn-based MOF (MOF-5) as a dopant we first prepare two (1 mg and 2 mg) TCP solutions for (Cs0.1(MA0.17FA0.83)0.9Pb(I0.83Br0.17)3) ((cesium (Cs), methylammonium (MA) and formamidinium (FA)) absorber layers in perovskite solar cell. The optical and morphological characteristics indicate better homogeneity with fewer voids, high luminescence, and excellent stability in the ambient atmosphere of the perovskite thin films. The fabricated device with 1 mg doping of MOF-5 possesses a high-efficiency power conversion efficiency (PCE) of 14% with current density (Jsc) 18.3 mA/cm², open-circuit voltage (Voc) 1.1, and the Fill-Factor (FF) 68. Furthermore, the device shows excellent stability by achieving 80% of the initial PCE for more than four weeks.

This work opens the prospect for other MOFs to be explored as a stabilizer for perovskites to get a highly stable, efficient, and intended for commercialization PSC.

ACKNOWLEDGMENTS

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REFERENCES


Anodic Tungsten Oxide: Synthesis & Photoelectrochemical Properties

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Abstract ID #NEE- 0320

Nowadays, photoelectrochemical water splitting under solar radiation is one of the most studied areas of science. Hydrogen gas in photoelectrochemical (PEC) systems is considered a renewable source of energy that can be produced from water on a large scale. Semiconducting materials are used as working electrodes in PEC cells due to their unique properties, such as light absorption ability and generation of charge carriers under illumination. Moreover, PEC systems often face many challenges in improving their overall energy conversion efficiency, especially at all wavelengths and shifting the absorption edge toward the visible light region [1, 2].

The search for effective photoelectrode materials operating under solar radiation is still ongoing. This talk will be focused on the control of optical and photoelectrochemical properties of anodic tungsten oxide layers by changing the anodizing conditions and post-treatment procedure.

Moreover, several ways to improve the photoelectrochemical properties of anodic WO₃ layers will also be discussed. One of the most promising strategies to enhance the photoresponse is the formation of a p-n heterojunction photocatalytic system that improves the separation and transfer of photogenerated charge carriers and shifts the absorption edge into the visible range [3, 4]. This strategy was implemented for anodic tungsten oxide-based junction with CuWO₄ and Fe₂O₃. Comprehensive characterization of materials was performed using SEM, XRD, XPS, UV-Vis DRS, Mott-Schottky analyses, and photoelectrochemical water splitting tests.

ACKNOWLEDGMENTS

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Novel Methods to Improve Nanostructured TiO$_2$ Properties for the Photocatalytic and Photoelectrocatalytic H$_2$ Generation

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Abstract ID #NEE- 0322

One of the most promising photosensitive materials that offer widespread applications is titanium dioxide (TiO$_2$). Due to suitable conduction and valence band edge positions, TiO$_2$ is used for the photolysis of water applied for renewable hydrogen production. In addition, TiO$_2$ in the forms of various nanostructures such as nanopowders, and anodic nanotubes/nanoporous array, with many times higher surface area in comparison to bulk materials, shows great potential for further modifications.

It is well known from photocatalytic (PC) and photoelectrocatalytic (PEC) studies on H$_2$ generation that the most common and efficient approach of titania modification is coupling with noble metal cocatalysts such as Pt, Ag, Au or their alloys [1]. Superior efficiency is usually assigned to several effects, such as Schottky barrier formation, cocatalytic properties, or surface plasmon resonance. The processes that might take place at the metal-semiconductor interface are complex. The type of the metal determines the character of the observed effect (e.g., the junction type depends on the difference in the work functions of metal and TiO$_2$), but also, more recently, size-dependent behavior was found to be an important aspect to be considered (e.g., single atoms, metal clusters, nanoparticles).

The well-designed architecture of nanostructured materials may lead to an extremely large interface area between noble metal and TiO$_2$. This has been found highly efficient by creating suitable electronic pathways to transport photogenerated electrons that lead to an enhanced spatial separation of holes and electrons and an improvement in the PC and PEC water splitting efficiency [2].

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REFERENCES


Nanomaterials for the Fabrication of Conductive Coatings on Power Contacts

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Abstract ID #NEE- 0342

Silver, as the material with the highest electrical and thermal conductivity, has been the most commonly used for the production of protective coatings for power contacts. However, its disadvantage is the high friction coefficient and significant plasticity, therefore it is easily damaged and deformed, which provides losses in the layers and corrosion of the substrates. These phenomena significantly reduce the “life” of power contacts. Recently, nickel nanoparticles (NPs) have been considered as a replacement for Ag NPs due to their lower price, better mechanical properties, and high electrical conductivity. However, Ni NPs are unstable under ambient conditions due to oxidation. As a suitable option to overcome the high cost of Ag and to prevent the spontaneous oxidation of nickel, bimetallic Ni-Ag NPs with the core-shell structure can be utilized [1, 2].

In our work, as a result of the transmetalation reaction, where the surface of the obtained Ni NPs acted as the reducing agent of silver ions, spherical Ni-Ag nanoparticles at average diameters of 220 nm were synthesized and applied for the fabrication of conductive coatings. The effect of the addition of noble metals NPs (silver or gold) as well as sintering temperature on the conductivity of metallic coatings were investigated. The obtained results show that the addition of both types of nanoparticles enhances the conductive properties of coatings compared to layers containing only Ni-Ag NPs. The conductivity of the sintered coatings increases with increasing sintering temperature. However, the most promising results were obtained for coatings dopped with silver nanoparticles. The layers with the highest conductivity (61 % of bulk nickel) were obtained after the sintering process at 300 °C, while from an economic point of view, the coatings with the conductivity of 44 % were obtained after the sintering at 200 °C.

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REFERENCES

ZrO$_2$-Based Nanopowders for Fuel Cells and Catalysis

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Abstract ID #NEE- 0364

Zirconia-based nanomaterials have attracted significant attention because of their diverse applications such as high temperature and corrosion-resistant coatings, radiation detectors, biological labels, solid oxide fuel cells and catalysts. To elaborate zirconia-based fuel cells and catalysts, ZrO$_2$ with tetragonal and cubic structures is most preferable. For the powders, both phases can be formed via ZrO$_2$ doping with subvalent elements. The required impurity charge compensation results in the formation of additional oxygen vacancies in the zirconia crystal lattice that stabilize tetragonal and/or cubic phases. As a consequence, higher ionic conductivity and catalytic activity can be achieved in zirconia-based materials.

In this work, the recent results on the effect of ZrO$_2$ doping with different subvalent elements (such as Y, Cu, Sc, Ce, etc...) on structural, optical, electric and catalytic properties of nanopowders and ceramics sintered on their basis are discussed. The powders were prepared by co-precipitation route and calcined at different temperatures (400-1100 °C). They were also used to produce the ceramic samples. Both powders and ceramic samples were investigated by means of diffuse reflectance, infrared spectroscopy, XRD, TEM, and EPR methods.

Among different ceramic samples, the most promising results were obtained from 8YSZ and 10Sc1CeSZ ceramics sintered at 1300-1550 °C. The ionic conductivity of 10Sc1CeSZ samples in the temperature range between 400 °C and 700 °C was found to be higher than that of traditional 8YSZ counterparts. It can reach about 0.046 S/cm at 600 °C due to close to zero grain resistance. By using additives like Al and Si, one can improve the sintering of the ceramics via the segregation of additives at the grain boundaries and, as consequence, their effect on the grain boundary conductivity. Twice decrease of grain boundary resistance and the increase of total ionic conductivity up to 0.033 S/cm at 600 °C were obtained. These results were compared with those obtained for the ceramics sintered from corresponding commercial powders.

It turned out that among different nanopowders, the most attractive results were obtained for the (Cu,Y)-ZrO$_2$ nanopowders. The effect of thermally stimulated spatial relocation of copper ions on the number of oxygen vacancies as well as monoclinic/tetragonal structure transformation was observed. A mechanism of the Cu incorporation in Y-ZrO$_2$ grains from Cu-related surface substances and Cu outward diffusion from the grain volume towards their surface stimulated by thermal treatment is proposed. It is shown that the monitoring of Cu content and Cu spatial localization permits to control the catalytic activity of the powders and to achieve, for instance, about 90% of the CO conversion in CO-PROX reaction in a wide temperature range. The comparison of the results obtained for similar commercial powders demonstrated the advantages of those developed in this work.

ACKNOWLEDGMENTS

This work was partly supported by the National Research Foundation of Ukraine from the state budget, project 2020.02/0380 «Structure transformation and non-equilibrium electron processes in wide bandgap metal oxides and their solid solutions» as well as by the National Academy of Sciences of Ukraine via the projects III-5-21 and all defenders of Ukraine that made this research possible.
Preparation and Characterization of Nanostructured TiO₂ for Industrial Wastewater Treatment

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Abstract ID #NEE- 0374

The application of illuminated semiconductors for the remediation of water contaminants has been used for a wide range of compounds and in most cases complete mineralization was achieved. The combination of UV irradiation and oxidants or catalysts (e.g. TiO₂) has attracted interest for the treatment of industrial wastewater as an alternative to conventional methods. Photocatalytic process (PCP) plays an important role in wastewater treatment; it is one of the most important methods used for complete mineralization of organic pollutants, urea, dyes and ammonia in the wastewater. The textile residual waters create environmental problems not only due to their colour but also because some dyes (azo dyes) may undergo natural anaerobic degradation to potentially carcinogenic amines.

This work involves preparation and characterization of nanostructured titanium dioxide, which were made from a sol-gel hydrolysis, autoclaving, and condensation of titanium isopropoxide in acetic acid solution. The prepared nanostructured titanium dioxide was characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Energy dispersive X-ray analysis (EDAX) and Fourier transform infrared (FTIR). The photocatalytic performance of TiO₂ nanoparticles were investigated by the decomposition of black 5 dye in an aqueous solution under UV light (254 nm) by different systems (UV/TiO₂, UV/TiO₂/H₂O₂, UV/TiO₂/ScO₉2, and UV/TiO₂/IIO₄) using a slurry photochemical reactor. The photocatalytic degradation of Black 5 was found to increase with increasing TiO₂ loading from 0.2 to 1.6 g/L. It was found that the photocatalytic degradation of Black 5 in the presence of irradiated TiO₂ was enhanced in the presence of low concentrations of inorganic oxidants. This may be due to the trapping of the photogenerated conduction band electrons from TiO₂ more efficiently than O₂.

The degradation efficiency of these catalytic systems could be arranged in ascending order as follows:

UV/TiO₂ < UV/TiO₂/H₂O₂ < UV/TiO₂/ScO₉2 < UV/TiO₂/IIO₄.

Efficiency parameters such as apparent quantum yield (Qₐpp) and electrical energy per order (EE/O) were estimated and compared for systems. It was found that Qₐpp for UV/TiO₂/IIO₄ system is higher than those for the other used systems. The EE/O for systems shows that periodate exhibited a low energy consumption compared to peroxide and persulfate.

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REFERENCES

Synergistic Antibacterial Effects of Cellulose:TiO$_2$ Nanocomposite Against Phytopathogens

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Abstract ID #NEE- 0382

The persistent use of pesticides and fertilizers in the field of agriculture causes soil pollution and even lead to health diseases like cancer (brain, breast and ovaries cancer). In order to reduce or eliminate the use of these traditional approaches for crop protection, the use of agricultural important antibacterial agents are improving the soil health and plant growth. The antibacterial agents possess the property to suppress the growth and ability of microbes to reproduce [1]. These agents are categorized into two groups, organic antibacterial agents (OA) and inorganic antibacterial agents (IA) [2]. One such potential OA is natural biopolymer Cellulose [3] which is an earth abundant material. The incorporation of inorganic nanoparticles can enhance the antimicrobial properties [4] of cellulose. Among many metal oxides, titanium dioxide nanoparticles (TiO$_2$ NPs) have proved its potential to be promising IA protecting plants against pathogens [5]. In this work, TiO$_2$ NPs were synthesized using hydrothermal method and nanocrystalline cellulose was synthesized by acid hydrolysis of commercially available microcrystalline cellulose (MCC). The commercial MCC are microfibers while the synthesized nanocrystalline cellulose (NCell) exhibit spherical nanoparticles. The nanocomposite TC (TiO$_2$/NCell) was prepared by incorporating TiO$_2$ NPs to enhance the antimicrobial property of nanocrystalline cellulose. All the synthesized NPs and the corresponding nanocomposite were characterized by using UV-Visible absorbance spectroscopy, X-ray diffraction, and transmission electron spectroscopy. The synthesized TiO$_2$ NPs exhibit elongated rods like sugarcane with average thickness of ~200 nm while the particle size of spherical nanocellulose is found to be ~15 nm. The XRD spectra of TiO$_2$ NPs showed a high peak of (101) plane at 2θ = 25.60 represent anatase form which is responsible for the formation of free radical. The antibacterial properties of synthesized nanoparticles (NPs) and nanocomposite (TC) were evaluated individually by using agar well diffusion method against phytopathogens: Xanthomonas campestris pv. campestris (Xcc), TiO$_2$/NCell) has proved its potential to be promising IA protecting plants against pathogens [5]. In this work, TiO$_2$ NPs were synthesized using hydrothermal method and nanocrystalline cellulose was synthesized by acid hydrolysis of commercially available microcrystalline cellulose (MCC). The commercial MCC are microfibers while the synthesized nanocrystalline cellulose (NCell) exhibit spherical nanoparticles. The nanocomposite TC (TiO$_2$/NCell) was prepared by incorporating TiO$_2$ NPs to enhance the antimicrobial property of nanocrystalline cellulose. All the synthesized NPs and the corresponding nanocomposite were characterized by using UV-Visible absorbance spectroscopy, X-ray diffraction, and transmission electron spectroscopy. The synthesized TiO$_2$ NPs exhibit elongated rods like sugarcane with average thickness of ~200 nm while the particle size of spherical nanocellulose is found to be ~15 nm. The XRD spectra of TiO$_2$ NPs showed a high peak of (101) plane at 2θ = 25.60 represent anatase form which is responsible for the formation of free radical. The antibacterial properties of synthesized nanoparticles (NPs) and nanocomposite (TC) were evaluated individually by using agar well diffusion method against phytopathogens: Xanthomonas campestris pv. campestris (Xcc), and Bacillus subtilis (BS). The outcomes of this study reveal that the nanocrystalline cellulose individually inhibits Xcc growth upto 24 hrs whereas nanocomposite TC inhibits the growth of Xcc upto 48 hrs. This manifests that the characterized nanocomposite TC has potentials for its future application to manage the bacterial disease in agriculture.

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Electrocatalytic Performance of Bimetallic Ni-Mo Alloy with Thermally Modulated Microstructure for Hydrogen Generation at Ultra-Low Overpotential in Acidic Media

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Abstract ID #NEE- 0387

Electrochemical water splitting has emerged as a promising route for renewable hydrogen generation in recent years, but still significant development of efficient and cost-effective catalysts is required to further reduce energy losses and the cost of materials for scalable and industrial applications. Herein, a highly efficient well-assembled bimetallic Ni-Mo electrocatalyst constructed on microporous nickel foam by potentiostatic electrodeposition method is reported which is capable enough to deliver high current densities of 50 mA/cm² at an overpotential below 100 mV vs. RHE in acidic medium. The variation in the electrochemical performance of the Ni-Mo alloy is largely attributed to microstructural variation as modulated by annealing temperature. This Binder free electrocatalyst with high Electrochemical Surface Area and improved physicochemical properties due to alloy formation at different temperatures facilitates electron transfer process resulting into an enhanced electrocatalytic activity.

ACKNOWLEDGMENTS

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REFERENCES


Starch-Containing Polylactide Nanocomposites

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Abstract ID #NEE- 0389

The rapid growth rate of the main indicators of development of high-tech industries and their restructuring into energy-saving and environmentally friendly technologies necessitate the creation of new and improvement of existing materials and production technologies.

Among the new materials, biodegradable polymers, in particular polylactide (PLA) and composites based on it, are the most widely used [1]. PLA is a biocompatible biodegradable thermoplastic polymer, which is characterized by good strength and rigidity, sufficiently high thermophysical properties. However, PLA has inherent properties that limit its application in many industries: increased fragility, low chemical resistance and resistance to thermal deformation [2]. At the same time, PLA has a higher cost compared to "classic" polymers. Therefore, there is a need to modify PLA by nanofillers, plasticizers, compatibilizers to give it the necessary properties for specific products and applications, as well as to reduce the cost.

In this work, starch-containing polylactide nanocomposites modified with epoxidized soybean oil (ESO) and filled with nanosized calcium carbonate were developed.

On the basis of the conducted researches the significant influence of components on physical-mechanical and thermophysical properties of polylactide materials is revealed. An increase in the modulus of elasticity of the obtained materials under the action of nanofiller and modifier, in particular, the highest values are characteristic of samples containing ESO, nanosized calcium carbonate and starch 10% by weight of each component. For all samples, regardless of the quantitative content of the components, there is a significant reduction in the modulus of high elasticity, which indicates a significant reduction in the fragility of polylactide nanocomposites.

A slight increase in the hardness of highly filled PLA materials was found. The increase in the content of ESO over 10% wt. leads to a decrease in surface hardness by 10-15%, apparently due to the plasticizing effect of ESO in PLA. It was found that the addition of starch and calcium carbonate to the PLA contributes to a significant increase in Vicat softening point of developed materials by 20-30 K.

Thermomechanical analysis revealed that the addition of starch has almost no effect on the nature of thermomechanical curves, at the same time the introduction of ESO leads to a stepwise appearance of thermomechanical curves, which indicates the transition of PLA to viscous state in two stages and shifting its melting temperature area of higher temperatures.

The obtained polylactide materials filled with nanodispersed calcium carbonate and starch and modified ESO can be used to obtain biodegradable products for the packaging, food and medical industries.

REFERENCES

Binary Ni$_{12}$P$_5$/BiVO$_4$ Photocatalyst for the Degradation of Organic Pollutants in Water

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Abstract ID #NEE- 0390

Water pollution has become a severe environmental problem on a global scale. It is caused by organic and inorganic materials such as pharmaceuticals, dyes, and heavy metals. The sources of these contaminants are the result of the industrialization as the runoffs from the nearest industries, agriculture, and domestic or rural communities end up in increasing pollutants level in the water. The stability of the pharmaceuticals makes it likely impossible for them to be removed from the water and the conventional treatment is not efficient and is made of non-biodegradable material. We prepared binary composite of nickel phosphide and bismuth vanadate (Ni$_{12}$P$_5$/BiVO$_4$) photocatalysts of various Ni$_{12}$P$_5$ loadings (0 – 1 wt. % Ni$_{12}$P$_5$) and their application as a photocatalyst were tested for ciprofloxacin and methylene blue degradation under simulated solar irradiation. The composite was characterized by X-Ray diffraction (XRD), UV-vis diffuse reflectance spectra (DRS), Zeta potential, scanning electron microscopy (SEM/EDS) and high-resolution transmission electron microscopy (HR-TEM). The results showed that the addition of Ni$_{12}$P$_5$ on BiVO$_4$ improves its photocatalytic activity, which is optimized for the sample containing 0.3 wt. % Ni$_{12}$P$_5$. This observation is probably attributed to the efficient separation of photogenerated charge carriers at the p-n junction formed at the Ni$_{12}$P$_5$-BiVO$_4$ interface. SMX degradation rate was found to increase by increasing catalyst concentration up to 500 mg/L or decreasing SMX concentration in the range of 250-2000 μg/L. The catalyst show high stability after several rounds of reuse.
Chalcogenide-based Heterostructures and Superlattices for Non-volatile Memory Applications

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Abstract ID #NEE- 0403

Chalcogenide-based phase change alloys are promising materials for optical and electronic memory applications. However, due to intrinsic properties of the alloys, the main challenge in material science is the optimization of memory writing times. The later are limited by the crystallization kinetic of the alloys. The next challenge is in the reduction of power consumption because erase process involves a melting of crystalline bit. There are several approaches to speed up the materials performance, such as pre-ordering of the amorphous state by the application of pre-programming pulses, doping of amorphous phase [1]. In this work, we propose to use GeSb₂Te₄-Sb₂Te₃ based heterostructures [2] and epitaxial layered Sb₂Te₃ thin films [3] to solve the issues.

Our results show that the use of the heterostructures can improve writing times of phase change memory devices. Microstructural study of memory cells in combination with ab initio molecular dynamical simulations reveal that the improvement in device performance is due to the enhancement in crystallization rate of amorphous GeSb₂Te₄ from crystalline Sb₂Te₃ surface. In addition, epitaxial 2D-like Sb₂Te₃ thin films are introduced as a novel active layer for memristive devices. The switching characteristics of those cells were dependent on the used electrode metals. Memory cells utilizing Ag and Cu electrodes showed forming-free characteristics and analog programmability, which can be used to mimic synaptic behaviors of biological systems.

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REFERENCES

Development of Nanophosphors Suitable for MicroLEDs

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Abstract ID #NEE-0406

During the last decade, high-performance displays, as well as fluorescent probes in nanomedicine or for specific shaping such as 3D printing with ink-jet techniques, have emerged, entailing the need for effective nanosized phosphors. This growing demand for nanophosphors has instigated research groups either to enhance existing nanophosphors synthesis protocols or to develop new synthesis and functionalization strategies for obtaining such efficient nanosized phosphors. Two distinct strategies can be used for their design, the bottom-up (direct assembly from molecules) or the top-down (size reduction to nanoscale) approaches.

In this talk, these two approaches will be illustrated through the presentation of Luminescent Group achievements of the past 10 years. In particular, nano Y_{3}Al_{5}O_{12}:Ce^{3+} (YAG:Ce) and quantum dots usable in microLEDs will be discussed.
Third Perovskite Revolution: Why, What and Why Not as Yet?

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Abstract ID #NEE- 0408

The discovery of the metal halide perovskite (MHP) as a photovoltaic (PV) absorber and the subsequent meteoritic rise of the efficiency of perovskite solar cells (PSC) are among the most important modern scientific breakthroughs.

Today the term ‘perovskite’ is used to designate the crystalline structure of a wide variety of ABX$_3$ ionic compounds. This name was coined for a specific mineral, calcium titanate (CaTiO$_3$). It was discovered in the Ural Mountains, Russia. The first sample of the mineral was transferred from Saint Petersburg to Berlin in 1839 by the Russian mineralogist Alexander Kämmerer, who gave the sample for further investigation to the German crystallographer Gustav Rose (1798–1873). Rose named the mineral after the Russian politician and mineralogist Lev Perovski. Lecture will start with a history of this discovery [1].

In 1987, the Nobel Prize in Physics was awarded to Georg Bednorz and Alex Müller for the discovery of High Temperature Superconductivity. Their Nobel Lecture was titled: “Perovskite-Type Oxides: The New Approach for High-Tc Superconductivity”. Another Nobel Prize in physics (2007) was awarded for the discovery of Giant Magnetoresistance (GMR), an abnormally high change in resistance of a conductor when it is placed in an external magnetic field. This quantum mechanical effect is observed in an alternating sequence of ferromagnetic and non-magnetic conductive nanolayers. The discovery of the GMR gave rise to an increased interest in finding related effects among bulk materials. Resistance change in an applied magnetic field several magnitudes higher than for GMR was observed in certain manganese perovskites. The observed phenomenon became known as colossal magnetoresistance (CMR).

I consider the development of highly efficient MHP photovoltaics as the third “perovskite revolution” of modern time. In 2007, PSC efficiency didn’t exceed 3 %, but today it is above 25 %.

Today’s manufacturing is dominated by silicon solar panels that have almost reached their maximum efficiency. The PSC development has changed the situation, paving the way to create the so-called tandem perovskite/silicon cells, with 30% already demonstrated. The prospect of overcoming 35% is now discussed. The main obstacle is that the PSC efficiency deteriorates quite rapidly under PV operation. Lecture will be finalized with a short review of our research toward the improvement of PSC operating stability.

REFERENCES

Easily Transferable Polydopamine Coatings for Energy Applications with Robust Mechanical Response

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The possible 2D-like arrangement of monomers in polydopamine films obtained by autoxidation of the dopamine at the air/water interface was recently reported [1]. While keeping their functional properties, the possible transferability of those films over a large variety of substrates is an attractive perspective of PDA film/coatings. We have prepared several films with tuned morphological and chemical properties. This presentation shows the growth control of the films obtained at the air/water interface with different dopamine concentrations, various pH, and stirring speeds and their transferability onto functional surfaces. The growth of the films was monitored in situ by spectroscopic reflectometry. The control of the growth process was achieved at the centimetre-scale level in terms of thickness homogeneity and chemical and structural characteristics of the obtained films. Transfer of the films onto substrates did not affect the homogeneity, foreshadowing an opportunity for large scalability of the process. The films are then transferred to different functional substrates showing improved photocatalytic response and promising applicability in water remediation and energy production.

Here we summarize all our recent findings on easily transferable polydopamine films on multiple functional substrates [2–4].

We present a thorough characterization of the films (SEM, HR-TEM, AFM, RAMAN and XRD), their applicability as free-standing materials (TEM and Nanoindentation), and their functional properties for energy production and environmental remediation (EIS, Photodegradation and Chronoamperometry).

We show the high quality of our films and the superior transferability towards energy applications. Our findings are a step forward toward understanding the PDA/semiconductor interface and its unique advantages for functional coatings.

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Conference Track: “Nanomaterials for Energy & Environment”
The Effect of the Substrate Orientation on the Electrical Properties of InGaP Solar Cells

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In this study, a detailed investigation was carried out on electrically active defects in n+-p-p+ GaInP solar cell structures grown on (100) GaAs substrates having misorientation angles (θS = 0°, 2°, 6°, 10°). The photovoltaic devices were investigated by using Current-Voltage (I-V), Capacitance-Voltage (C-V) and Deep Level Transient Spectroscopy (DLTS) techniques in the temperature range 10 K - 450 K. The n+-p-p+ structures were grown by metalorganic chemical vapour deposition (MOCVD) technique. Ohmic contacts to the n+ and p+ layers were formed on these structures by metallization process. The ideality factor values, which were obtained from I-V characteristics, were found to decrease with increasing temperature. The ideality factor was found to be greater than 1.20 for all temperatures, indicating that the generation recombination mechanism was dominant over the diffusion mechanism. From CV measurements, the free carrier concentrations were calculated. The sample grown on 60 off has the highest free carrier concentration while sample grown on exact (100) has the lowest free carrier concentration. DLTS and Laplace DLTS measurements showed two traps including shallow and deep traps ringing from (0.027eV to 0.39eV) for all samples except the samples grown on 20 off-oriented GaAs substrates which have only one trap with activation energy(0.05 eV). Our findings suggest that the optimum misorientation of GaAs is 20 off.
Role of Porous Nanocomposite in Environmental Monitoring and Remediation

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The global increase in the quality of life accompanied by demand for emerging pollutants such as pharmaceutical and personal care products has introduced a new threat to an already scarce natural resource for humans, which is water. These also drew considerable attention over the last decades due to the number of emerging pollutants detected in aqueous environment compartments. This study reports the application of porous nanomaterials the removal of ten selected emerging contaminants (fluoroquinolone antibiotics, parabens, anticonvulsants, and β-blockers) in water systems. Magnetic mesoporous carbon/β-cyclodextrin–chitosan, magnetic cellulose-chitosan hydrogel, and zeolitic imidazolate framework-67@magnetic porous porphyrin organic polymer nanocomposites were used as an adsorbent in the adsorption process. The adsorption process was optimized using central composite design. Under the optimum conditions, the removal efficiencies ranged from 90-100%, 95-99.7%, and 98-101% for anticonvulsants and β-blockers, fluoroquinolone, and parabens, respectively. The feasibility of the method in real samples was assessed by analysis of river water, tap water, and wastewater samples. The recoveries for the investigated analytes in the real samples ranged from 93.5 to 98.8%, with %RSDs under 4%.
The Role of Interfaces in Composite Nanomaterials for Energy Conversion

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Abstract ID #NEE- 0440

Composite nanostructures can be efficiently applied for Sunlight detection and conversion and, more in general, for energy harvesting and generation of solar fuels. In most applied systems, like photodetectors, excitonic solar cells, and (photo)-electrochemical cells to produce solar fuels, nanomaterials can play a critical role in boosting photoconversion efficiency by ameliorating the processes of charge photogeneration, exciton dissociation and charge transport. A critical role in such processes is played by the structure and quality of the interface, which needs to be properly assembled to obtain the desired functionality. Several strategies can be pursued to maximize energy harvesting and storage, including broadening light absorbance to reduce solar light losses, fastening exciton dissociation and charge injection from the photoactive medium to the charge transporting materials, and reducing charge recombination during charge transport and collection at the electrodes. In this lecture, a few examples of application of nanocomposites will be discussed, including all-oxide coaxial p-n junction nanowire photodetectors and solar cells, core-shell quantum dot fluorophores for high-efficiency luminescent solar concentrators, composite sulfides for hydrogen generation, and oriented carbon nanotube forest dispersed in polymer matrix as efficient low-temperature thermoelectric composite. Emphasis will be given to the role of interface engineering in improving the efficiency of energy conversion in different systems, spanning from electric power generation from Sunlight to chemical fuel production, to conversion of heat lost through thermoelectric materials.

REFERENCES

Role of Heterojunctions in Metal Oxide Heterostructures for Energy and Environmental Applications

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Heterostructures made from metal oxide semiconductors are fundamental for the development of high-performance gas sensors and electrocatalysts, for examples. In this lecture I will introduce hierarchical heterostructures composed of p-, n-type and insulating metal oxide shells. Precisely controlled films of alternating metal oxides can be uniformly deposited onto the inner and outer walls of the CNTs and onto mesoporous substrates by atomic layer deposition. The morphological, microstructural and electrical characteristics of the heterostructures were thoroughly investigated. Electrical resistance measurements highlighted the large influence of the metal oxides thickness and charge carriers types, suggesting that the conductivity of the electrodes are dominated by Schottky barrier junctions across the heterojunctions. The behavior of the heterostructured electrodes in sensors and in electrocatalysis applications was investigated for low concentrations of volatile organic compounds and pollutants, and the oxygen evolution reaction in acidic media, respectively. For examples, the gas sensing response of the heterostructures showed a strong dependence on the thickness of the metal oxide shell layers and the type of heterostructures formed. On the other hand, the electrocatalytic performances are strongly related to the surface catalyst/stabilization layer and the electrical conductivity of the heterostructured electrode. On the basis of the morphological, microstructural and electrical characterization, and electrode performances, the mechanisms which account for the performances of our heterostructured electrodes will be correlated and discussed.

REFERENCES
Metal Nanoparticles in Natural Deep Eutectic Solvent (NDES)

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The aim of the research was to verify the possibility of obtaining suspensions of metal nanoparticles (Ag, Au, Cu) using natural deeply eutectic solvents (NDES) and to study their physicochemical properties. The components of NDES, among others, sugars, amino acids, alcohols were compounds with reducing properties and stabilizing properties [1]. By choosing the components of NDESs, it was possible to obtain metal nanoparticles without introducing additional reducing agents, often toxic to the environment. In addition, the presence of compounds that are hydrogen bond donors and acceptors resulted in solvents without the addition of water. The selection of NDES components was crucial both in terms of the size of the nanoparticles obtained and in obtaining stable suspensions of silver, gold and copper nanoparticles [2, 3].

Based on the analysis of the literature, the possibility of obtaining nanoparticles was confirmed, but limited information in the analysis of the composition of NDES on the properties of the obtained nanoparticles was observed, as well as the lack of information on the possibility of obtaining different nanoparticles [4]. In addition, it was observed that the added NDES act as a stabilizer/reducer, and the solvent in the majority of publications remained water. As it is well known that metal nanoparticles exhibit antimicrobial properties, obtaining them in NDESs also allowed them to be used as anhydrous additives with biocidal effects [5-7].

In the first stage of the research, mixtures of NDES were obtained, based on which those with the desired parameters, directly affecting the quality of the obtained nanoparticles, i.e. reducing and stabilizing properties, were selected. The physicochemical properties of the solvents were studied, including viscosity, pH, stability over time, etc. In the second stage, a methodology was developed for obtaining metal nanoparticles, i.e. silver, copper and gold, using selected NDES. In the third part of the research, after determining the basic physicochemical properties, the materials were analysed by antimicrobial tests.

The nanoparticles had an average size of about 80-400 nm (determined by DLS method), and depending on the composition of the NDES, the size of the nanoparticles varied. The NDESs exhibited a double function as a reaction medium and a directing agent for the shape and size of the nanoparticles. The selected natural deep eutectic solvents were characterized by stability exceeding 6 months, pH of the solutions ranging from 4 to 7, and viscosity ranging from 90 to 5·10$^4$ cP.

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Metal nanoparticles, natural deep eutectic solvents, NDES.

REFERENCES


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TRACK 11

“NANOBIO MEDICAL RESEARCH & APPLICATIONS”
Exploiting Plasmid-Mediated Resistance: Design of Small-Molecule Inhibitors for the Disruption of the Kid-Kis Toxin-Antitoxin System in Plasmid R1

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Abstract ID #NRA-003

Antibiotic resistance is one of the leading challenges to public health today, and a primary contributor to the rapid rise of resistance is plasmids, which facilitate the spread of multi-drug resistance genes within bacterial populations through horizontal gene transfer [1]. Therefore, plasmids are critical targets to prevent the rapid spread of antibiotic resistance. In particular, low-copy number plasmids often contain toxin-antitoxin systems that act lethally when activated, so due to the role of toxin-antitoxin systems in facilitating internal cell death, the disruption of the protein-protein interaction between the toxin and the antitoxin may be a promising novel target for antibiotic development [2, 3]. Key interacting regions of the Kid-Kis toxin-antitoxin interaction were identified as binding sites for the de-novo design of small-molecule inhibitors using the webserver LEA3D [4].

To predict the activity of novel inhibitors, a QSAR classification model was constructed with OCHEM using published experimental data on a related system. The most promising inhibitors with drug-like properties were molecules targeting the Glu66 to Arg72 region of the Kis antitoxin, as four out of five inhibitors were classified as active compounds [5]. Calculations for Gibbs free energy ($\Delta G = 0.000000252$) and $pKd (p = 0.000459)$ showed statistically significant binding affinity compared to control molecules with no known affinity for the target, representing a significant binding specificity towards the target interaction region. In the fight against antibiotic resistance, the design of small-molecule inhibitors targeting toxin-antitoxin systems may be an important discovery for the selective targeting of plasmid-mediated resistance through the application of internal mechanisms toward antibiotic development.

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REFERENCES

Nanoscale Calcification of the Dura Mater

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Abstract ID #NRA-004

Intracranial calcification can manifest physiological (age-related) and pathological processes in the brain's structures [1]. In accordance with autopsies, the prevalence of calcifications, including microscopic, reaches 72% [2]. Based on the computer tomography (CT), the calcification of the dura mater (DM) is observed in 12.5% of the adult population [3]. They are often localized in the falk cerebri (26.8%) [4] and in a young population, should be a reason for differential diagnosis with tumors [5]. It should be noted that the phenomenon of pathological biomineralization is one of the features of DM tumors (intracranial meningiomas) [6, 7]. After cerebral or spinal operative procedures, it is imperative to provide a complete and watertight dural closure to minimize the risks of cerebrospinal fluid fistulas, infections, brain herniation, cortical scarring, and adhesions [8]. The study of morphological and physiological features of the DM will create a basis for the development of new materials for bioplastics and regenerative medicine.

The focus of this work is to study the structural and elemental composition of inclusions in DM tissue. Thirty specimens of the DM obtained during autopsies at Sumy Regional Hospital were involved in our research protocol. Based on the histological investigation, we split the samples into two groups (15 samples each): with proof of the biomineralization (group M) and control (group C). To confirm the presence of calcium compounds, we stained the samples with von Cossa and alizarin red assays and performed Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS).

The staining of DM tissue with alizarin red confirmed the presence of calcium compounds (orange-red color) and inorganic iron (purple color) in all samples of group M. SEM data demonstrated the calcification in eleven samples from group M with the size ranging from 1 to 50 μm. EDS characterization revealed the prevalence of Ca and P lines with Ca/P ratio, specific to hydroxyapatite (Ca$_3$(PO$_4$)$_2$(OH)$_2$).

Most normal DM samples contain the biomineral deposits with Crystal-chemical and phase composition corresponding to calcium hydroxyapatite and extremely small size (from 1 to 50 μm). The physiological role of DM calcifications remains unclear and requires further research, but the calcified tissues should be a relevant model for biocomposite material development.

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REFERENCES


Conference Track: “Nanobiomedical Research & Applications”
The Study of the Nanocrystalline Structure of Psammoma Bodies of Serous Ovarian Carcinoma for Practical Application in the Diagnostics

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Abstract ID #NRA-009

Psammoma Bodies (PBs) are very important clinical and morphological diagnostics criteria for serous ovarian cancer. These calcified formations have a lamellar structure [1, 2]. The initiation of PBs development appears at the early stages of ovarian carcinogenesis, which is vital for the early diagnosis of ovarian tumors [3]. The incidence of these calcifications is about 100% and 50% for low-and high-grade serous ovarian cancers, respectively [3, 4]. It was also found that PBs larger than 200 μm could be identified by ultrasound [5].

Our research aimed to study the nanocrystalline structure of psammoma cells of serous ovarian carcinoma for practical application in diagnostics. We have analyzed 30 samples of serous ovarian carcinoma using histology (hematoxylin-eosin staining), immunohistochemistry (Osteopontin and Amyloid Fibrils OC), and Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS). The graphical representation of statistical analysis was performed in Microsoft Office Excel 2016 with the addon Attestat (version 12.0.5).

The immunohistochemistry revealed the accumulation of Osteopontin and Amyloid Fibrils OC on the surface of PBs. Osteopontin covered the surface of calcifications with more intense accumulation at the edges and between the lamellae. It pointed out that hydroxyapatite was the main mineral component of these formations. The Amyloid Fibrils OC was accumulated on the surface of lamellar structures with much higher intensity on the periphery, which indicates the presence of this protein in the PBs. SEM revealed that PBs were particles of different sizes, round shapes, and lamellar structures. The phase-crystal structure of PBs was represented by calcium and phosphorus compounds, the ratio of which corresponded to the hydroxyapatite. According to the distribution maps of the elements, we found the accumulation of calcium (Ca), phosphorus (P), and oxygen (O) at the sites of localization of calcified particles. Carbon (C) was distributed evenly in the field of the scanning sample with no signs of accumulation in the localization of biominerals. It has been found that the number of PBs in ovarian tumor tissue varies from 1 to 200 per sample, as well as their diameter – from 12.6 μm to 493.7 μm. All calcifications were divided into three groups based on their size: large – more than 200 μm (detectable by ultrasound), medium – 71 – 199 μm, and small – up to 70 μm. PBs had a lamellar structure with the mean thickness of the lamellae of 0.65 μm (± 0.02) and the thickness of the inter-lamellar layer of 3.7 μm (± 0.17). We detected a strong correlation between the thickness of the inter-lamellar layer and the size of PBs (r = 0.79; p <0.001).

Therefore, based on the nanocrystalline structure and morphometric characteristics of PBs, this pattern can be used in practice for the early diagnosis of serous ovarian cancer.

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Conference Track: “Nanobiomedical Research & Applications”
REFERENCES


Magnetically Guided pH-Sensitive TiO$_2$ Nanoparticles for Delivery of Chemotherapeutics

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Abstract ID #NRA-0011

Stimulus-responsive drug delivery is the much sought-after technique to ensure targeted drug delivery. A novel approach was followed to synthesize magnetically sensitive Pegylated iron-supplement capped rutile titanium dioxide (TiO$_2$) nanoparticles (NPs). The decision of PEGylation and using iron supplement was made to enhance the biocompatibility of the NPs. FericipXT is the iron supplement that was coated onto the rutile TiO$_2$ NPs. The antineoplastic drug Imatinib was loaded onto the NPs and its in-vitro release profile was investigated under acidic, neutral and basic pH conditions. X-Ray Diffraction analysis (XRD) confirmed the successful synthesis of rutile TiO$_2$ NPs followed by iron-supplement coating and a PEG (polyethylene glycol) layer. Despite the crystalline nature of the drug, it was loaded in its amorphous form onto the NPs. High-resolution Transmission Electron Microscopy (HRTEM) studies have shown an increasing trend in the size of rutile TiO$_2$ NPs upon coating followed by PEGylation and drug loading. Vibrating-Sample Magnetometry (VSM) studies confirmed the magnetic responsiveness of the synthesized NPs which validate that the NPs can be guided to a specific location via external magnetic fields. The coating of the iron supplement greatly modified the magnetic responsiveness of the otherwise diamagnetic TiO$_2$ NPs. The in-vitro drug release study showed maximal release in acidic media with pegylated NPs exhibiting controlled drug release performance. This is a much-appreciated release behaviour as the pH around cancerous tissue is generally acidic. Thus, the NPs synthesized by us possess significant potential to be used for targeted delivery and controlled release of chemotherapeutic agents thereby providing the least side effects.

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REFERENCES

The Structure of Nanocrystalline Apatite from the Breast Cancer

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Abstract ID #NRA-0012

Detection of microcalcifications in the breast by mammography is of great importance in the diagnostics of breast cancer, especially at the early stages [1]. Breast cancer microcalcifications usually are associated with degenerative-necrotic changes in tumor tissue [2]. Microcalcifications in the breast correlate with a worse prognosis, primarily because of a higher incidence of lymph node invasion and rapid metastasis [3]. Osteopontin, which is closely related to hydroxyapatite, plays a role in the biomineralization that occurs in certain breast cancers [4].

This research aims to establish the composition and morphology of biomineral deposits of breast cancer. Our study examined 30 specimens of breast cancer obtained during surgery at Sumy Regional Oncological Hospital. The samples were analyzed by histology (hematoxylin-eosin staining), Scanning Electron Microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), and Transmission Electron Microscopy (TEM).

Histological examination of breast cancer samples revealed the presence of microcalcifications in the form of dark blue deposits of the round and irregular shapes of different sizes. A positive reaction to von Koss staining indicates the presence of calcium phosphate compounds in their composition. We also confirmed the presence of round calcifications using SEM. Most calcifications are damaged during sample preparation but retain the characteristics of the previous round layered structure. According to the element distribution maps and the Ca/P ratio from the X-ray microanalysis spectra, the mineral deposit had a calcium phosphate (apatite) composition and the Ca/P ratio from the X-ray microanalysis spectra at selected points.

High-resolution TEM imaging has shown some structural and morphological features of breast cancer apatite crystals, which were not detected by other methods. According to TEM, crystalline nanoparticles were polydisperse (had different sizes) with minor size variations (3-20 nm). Nanocrystals of breast cancer calcifications formed the polycrystalline mechanically stable agglomerates with 100 – 300 nm sizes. At the same time, there were no signs of recrystallization with a noticeable increase in the size of individual components of these agglomerates.

Further studies will be focused on the diagnostic potential of microcalcifications for the early diagnosis of breast cancer.

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REFERENCES


Photocatalytic and Antioxidant Properties of Nanoceria at UV Irradiation/Pre-irradiation

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Abstract ID #NRA-0030

Reactive oxygen species (ROS) such as hydrogen peroxide (H$_2$O$_2$), superoxide anions (O$_2^-$) and hydroxyl radicals (·OH) are indispensable for signal transmission and immune response in living cells. However, the concentration of ROS in a cell needs to be under strict regulation due to strong destructive effect of the most active types of ROS (such as ·OH) on the DNA and lipid membranes. Recently a new type of antioxidant materials able to reversible ROS neutralization based on nanocrystals with ions of variable valence (so-called nanozymes) was proposed. Nanoceria (CeO$_{2-x}$) is a most well-known antioxidant nanocrystal due to its high ROS scavenging efficiency in water solutions and living cells determined by defect and electron structure of these nanocrystals. At the same time, the mechanisms controlling its antioxidant activity are still under discussion [1, 2]. Moreover, there are some reports on prooxidant action of nanoceria as well.

In order to reveal the ways to control the type and efficiency of redox activity of nanoceria, we have obtained colloidal solutions of ceria nanoparticles of different sizes (2 nm and 10 nm). The NPs were characterized using the methods of transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Both XPS and luminescence spectroscopy methods have revealed the high content of Ce$^{3+}$ ions in obtained nanoceria. UV irradiation of nanoceria solutions leads to increase of Ce$^{3+}$ content in nanoceria due to Ce$^{4+} \rightarrow$ Ce$^{3+}$ reduction. Capture of electrons by Ce$^{4+}$ ions and holes by oxygen ions leads to formation of additional Ce$^{3+}$-Vo-Ce$^{3+}$ complexes, which are responsible for antioxidant activity of nanoceria [3]. We have shown that the content of hydroxyl radicals in X-ray irradiated water solutions decreased sufficiently in the presence of pre-irradiated nanoceria compared to initial (non-irradiated) nanoceria samples. Moreover, nanoceria hampers the process of epinephrine autoxidation due to effective O$_2^-$ scavenging and UV pre-irradiation of nanoceria water solutions improves its O$_2^-$ scavenging ability. At the same time, during continuous UV irradiation nanoceria demonstrates prooxidant photocatalytic action under UV irradiation leading to increase of ROS content (both hydroxyl radicals and superoxide anions) in water solutions. In this way, UV irradiation of nanoceria before (pre-irradiation) or during nanoceria-ROS interaction can lead either to higher prooxidant or higher antioxidant activity of nanoceria opening the way for obtaining nanoparticles with pre-determined and switchable redox action.

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REFERENCES

Control of ROS-Regulating Properties of (Gd,Y)VO₄:Eu³⁺ Nanoparticles

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The excess generation of reactive oxygen species (ROS) in the level of cells is revealed to induce an array of physiopathologic outcomes, including genotoxicity, apoptosis, necrosis, inflammation, fibrosis, metaplasia, hypertrophy, and carcinogenesis. This finding provokes the development of novel strategies in medicine, so-called ROS-regulating nanomedicine with the use of ROS-upregulating (ROS induced toxic therapy) and downregulating (antioxidant therapy) nanomaterials [1]. In this work, we analyze the effect of pretreatment of (Gd,Y)VO₄:Eu³⁺ nanoparticles (NPs) on their ROS regulating ability. Both ROS-up- and ROS-downregulating properties have been revealed for (Gd,Y)VO₄:Eu³⁺ NPs depending on pretreatment conditions: UV-light irradiation or storage in the darkness. It was found that (Gd,Y)VO₄:Eu³⁺ NPs of about 2 nm size effectively scavenge hydroxyl radicals, superoxide anions, hydrogen peroxide, peroxyl radicals and remarkably reduce the lipopolysaccharide–induced ROS generation in rat leukocytes [2]. The antioxidant action of (Gd,Y)VO₄:Eu³⁺ NPs is found to be associated with the high amount of V⁴⁺ and V³⁺ ions stabilizing oxygen vacancies in the crystal lattice and reversible switching V³⁺↔V⁴⁺ and V⁴⁺↔V⁵⁺ vanadium oxidation states [2, 3]. At the same time, UV-light pre-treated (Gd,Y)VO₄:Eu³⁺ NPs revealed strong ROS producing properties both in cell-free and biological milieu and under X-ray exposure, as well [2, 3]. The mechanism of the pro-oxidant action is also associated with the defect structure of NPs and trapping of photo-induced holes on the local levels during UV-light pretreatment with a subsequent diffusion to the surface of NPs, interaction with H₂O molecules and hydroxyl radicals production.

Thus, pretreatment conditions can control ROS-regulating properties of (Gd,Y)VO₄:Eu³⁺ NPs making them promising for biomedical applications such as radiotherapy, which will ensue a new approach in malignant cell treatment.

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Designing Patches with Nano and Microfiber Membranes Delivering Topically Oil and Drugs for Atopic Skin Treatment

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Many widespread skin problems including eczema affect people all over the world. Most of the treatment methods for atopic dermatitis (AD) are focused on increasing skin moisture and protecting from bacterial infection and external irritation. Topical and transdermal treatments have specific requirements for drug delivery. Breathability, flexibility, good mechanical properties, biocompatibility, and efficacy are important for the patches used for skin. In AD skin moisture is highly decreased due to transepidermal water loss, therefore patches, which can increase hydration in the long-term application are desired. In our studies, we used electrospun polymer membranes with a porosity above 90%. Electrospun fibers are reported to be applicable as membrane loaded with natural oils, beneficial especially for eczema [1]. We manufactured nano- and microfibers from various polymers (PVB, PCL, PHBV, PI, PA6, PS). The advantage of electrospun membranes is a high surface-to-volume ratio, which is beneficial in skin patches [2]. Additionally, we apply various natural oils such as evening primrose, blackcurrant seeds, or hemp oil [3-5] to verify experimentally and via numerical simulations their delivery to the skin. We show that oil spreading and transport in patches depends on the geometry of the fibers, their surface properties porosity, and pore sizes. These results give an enormous possibility of controlling the oil and drugs delivery to the skin, not only with AD problems. Furthermore, we performed in vivo skin hydration test with natural oil applied on the electrospun membranes on the skin to investigate hydration increase according to the design of the patches. In conclusion, we have shown the novel and easy method to apply, for controlled transdermal delivery and moisturization through electrospun patches to improve the comfort and lifestyle of people with eczema.

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Size-Dependent Effect of CeO$_2$ Nanoparticles on ROS Generation in Red Blood Cells

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Highly reactive free radicals such as reactive oxygen species (ROS) and reactive nitrogen species (RNS) are involved in the pathogenesis of multiple diseases. Thus, antioxidant therapy has been under investigation for decades. However, it still has numerous challenges, including inadequate bioavailability of exogenous antioxidants, their insufficient stability, lack of targeted delivery, and poor efficiency [1]. Nanoceria (cerium oxide nanoparticles) are known to be potent antioxidants, which makes them good anti-inflammatory agents and stimulators of tissue repair and regeneration [2]. The anti-pro-oxidant properties of nanoparticles are known to depend sufficiently on the experimental conditions, and the results obtained for cell-free media and various cell cultures can strongly differ. Accumulating evidence indicates that erythrocytes can be used as an efficient model to assess the toxicity profile of nanosized materials and mechanisms of their adverse effects on cells. The aim of current research was to assess reactive oxygen species (ROS) production-stimulating properties of CeO$_2$ nanoparticles in red blood cells. Two types of cerium oxide nanoparticles (2 nm and 10 nm) were used in this experimental study. Erythrocyte suspensions prepared from intact blood samples (n = 6) incubated with both types of CeO$_2$ nanoparticles (0-10-20-40-100-200 mg/L) were stained with 2’,7’-dichlorodihydrofluorescein diacetate (H$_2$DCFDA) to determine intracellular ROS levels. The ROS concentrations inside the erythrocytes were judged by dichlorofluorescein (DCF) fluorescence acquired using BD FACS Canto™ II flow cytometer (Becton Dickinson, USA) [3]. The quantitative analysis of ROS production was performed by comparing the mean fluorescence intensity (MFI) of DCF. At concentrations of 100 mg/L and below, smaller (2 nm) and larger (10 nm) CeO$_2$ nanoparticles had no impact on ROS production. The highest used concentrations (200 mg/L) promoted ROS overproduction only in case of small-sized nanoparticles. A decrease in the size of ceria nanoparticle favors Ce$^{4+}$ $\rightarrow$ Ce$^{3+}$ reduction accompanied by formation of oxygen vacancies on the surface and in the volume of nanoparticles. Thus, smaller nanoparticles are generally considered to be more redox active than the larger ones. This explains our observations on the ability of the small-sized nanoparticles to affect the redox homeostasis of erythrocytes in contrast to the nanoparticles of 10 nm. Our observations show that nanoceria-induced ROS generation in erythrocytes depends on nanoparticle size. This study confirms that CeO$_2$-associated toxicity is mediated by excess ROS generation and oxidative stress. We believe that erythrocytes are promising models in nanotoxicology.

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REFERENCES

Assessing the Toxicity of TiO₂ Nanoparticles with a Different Ti³⁺ (Ti²⁺) / Ti⁴⁺ Ratio

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Abstract ID #NRA-0039

Nanomedicine is an emerging field of nanotechnology, which is revolutionizing healthcare worldwide [1]. Among nanostructured materials, whose biomedical application is under investigation, nano-sized titanium dioxide seems to be promising. TiO₂ nanoparticles have been used as biosensors, implant coatings, antibacterial agents, cell imaging agents, drug delivery systems, agents for photodynamic therapy, etc. [2]. In many studies evidence has been provided that nano-sized titanium dioxide toxicity is mediated by reactive oxygen species (ROS) overproduction. Thus, biosafety screening of newly synthesized TiO₂-x nanoparticles should include tests on ROS induction. Thus, the aim of this study was to analyze ROS-generating effects of TiO₂-x nanoparticles on erythrocytes in vitro. In this study, we show that Ti³⁺ (Ti⁵⁺)/Ti⁴⁺ ratio determines the toxicity of TiO₂-x nanoparticles. Using the original route, two types of titanium oxide nanoparticles with the same size of 5 nm, but different Ti³⁺(Ti⁵⁺)/ Ti⁴⁺ ratios in the crystal lattice were synthesized. In 1-TiO₂-x nanoparticles, about half of titanium atoms were in the lower valence state, 54% Ti³⁺ and 46% Ti⁴⁺, as it was revealed by the XPS analysis. The relative amount of Ti⁴⁺ and Ti³⁺ in the crystal lattice of 2-TiO₂-x nanoparticles was calculated to be 63% and 37%, respectively. Ti₂⁺ was not detected. Intact blood obtained from 6 WAG rats was incubated with both TiO₂-x nanoparticles (0-10-20-40-100-200 mg/L) for 24 h. Erythrocyte suspensions prepared from the incubated blood samples were stained with 2',7'-dichlorodihydrofluorescein diacetate (H₂DCFDA) to examine the redox state of cells. Intraerythrocytic ROS levels were quantified by dichlorofluorescein (DCF) fluorescence with the help of BD FACS Canto™ II flow cytometer (Becton Dickinson, USA) [3]. Treatment of erythrocytes with two types of TiO₂ nanoparticles at concentrations of up to 100 mg/L did not alter DCF fluorescence suggesting no influence of ROS generation. Meanwhile, 200 mg/L 1-TiO₂-x nanoparticles statistically significantly (p = 0.0002) increased ROS production in erythrocytes, which was not observed in case of 2-TiO₂-x nanoparticles. One of the possible mechanisms responsible for ROS bursts in this case is a release of metal ions and mixing into redox cycling and chemocatalysis via the Fenton and Huber-Weiss reactions. For TiO₂-x nanoparticles, oxygen vacancies compensated by Ti³⁺ or Ti⁵⁺ ions are considered to be reactive sites with an effective adsorption of O₂, H₂O₂, H₂O and other small molecules and subsequent production of different kinds of ROS with a participation of electrons stored at VO or Ti⁴⁺ and Ti³⁺ ions. This study reveals that TiO₂-x nanoparticles are characterized by quite good biocompatibility against red blood cells. Their toxicity is at least partially associated with non-mitochondrial ROS generation. Ti³⁺ (Ti⁵⁺)/Ti⁴⁺ ratio determines the toxicity of TiO₂-x nanoparticles.

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Mycosynthesized Silver and Zinc Oxide Nanoparticles: Their Characteristic, Antimicrobial and Antibiofilm Activities

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Due to increasing resistance of bacteria to conventional antibiotics, it is necessary to develop new antimicrobial agents [1]. Metal NPs exhibit unique properties that affect their antibacterial activities, and make them potential solution to combat bacterial pathogens [2]. The objective of this study was the mycosynthesis of zinc oxide (ZnONPs) and silver (AgNPs) nanoparticles using extracts of different fungal species. Briefly, AgNPs were synthesized by using AgNO₃ as precursor, then reaction mixture was light induced. ZnONPs were formulated using two. The first method included mixture of the fungal extract, ZnSO₄ and NaOH in a ratio of 1:1:1 (v/v/v), then the mixture was heated at 40 °C. The second method, the pH of the mixture of fungal extract and ZnSO₄ (1:1, v/v) was adjusted at 8 or 11 with NaOH. The formation of NPs was verified using UV-Vis spectrometry in the wavelength 200-700 nm. The shape and size, elemental composition, capping molecules, crystal structure of the NPs were determined using Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), respectively. The antimicrobial activity of nanoparticles against bacteria was evaluated by determination of the minimum inhibitory (MIC) and minimum biocidal (MBC) concentrations. Antibiofilm activity of AgNPs were evaluated by crystal violet assay. Based on results from Uv-Vis spectroscopy fungal strains were selected for further synthesis. Maximum absorbance peaks in range 420-450 nm were detected for AgNPs synthesized from F. culmorum, F. solani and F. oxysporum. Absorbance peaks at wavelength 330-370 nm confirmed formation of ZnONPs by A. niger, F. graminearum, F. solani using first synthesis method and by F. culmorum, F. oxysporum and F. solani using second synthesis method. TEM analysis revealed formation of small (8-25 nm) AgNPs and larger (120-370 nm) ZnONPs, whereas EDS analysis displayed Ag and Zn as main components, respectively. According to FT-IR results, the surface of NPs was capped with various biomolecules. XRD analysis confirmed crystalline structure of both kinds of NPs. MIC were determined at 16-512 µg mL⁻¹ for AgNPs and > 128 µg mL⁻¹ for ZnONPs. The highest antimicrobial activity was determined for AgNPs from F. culmorum, MIC and MBC were in range 16-64 and 32-128 µg mL⁻¹, respectively. These NPs were selected for antibiofilm formation assay. The biofilm formation by P. aeruginosa and K. pneumoniae was significantly reduced after treatment with 16 and 64 µg mL⁻¹ of AgNPs, respectively. Maximum tested concentration (512 µg mL⁻¹) of AgNPs reduced biofilm formation by S. aureus by 50%. Results indicate that mycosynthesized ZnONPs and AgNPs exhibit unique properties (small size, various shapes) that can influence their ability to combat bacteria. Furthermore, NPs display the potential to be used as antimicrobial agents for widespread biomedical or industrial applications.

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Amphi-PIC J-Aggregate – Protein Complexes: Stability in Blood and Toxicity to Cell Cultures

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Highly molecular ordered aggregates, called J-aggregates, are low-dimensional crystals, whose optical properties are caused by the delocalization of electronic excitations over some segments with Frenkel excitons formation. Depending on the molecular arrangement, the excitonic band can be the red-shifted narrow one (called J-band) or the blue-shifted wide one (called H-band). Currently, significant interest in J-aggregates is associated with using the strong bathochromic shift of the J-band to create fluorescent probes effectively absorbing and emitting light in the near infrared (NIR) region. It is important to note that some J-aggregates reveal high absorption and fluorescence not only in the already traditional NIR-I region (700 – 900 nm) but also in NIR-II (1000 – 1500 nm), where the depth of light penetration into tissues is much greater.

The application of J-aggregates in biological systems requires the study of their stability and toxicity. It is known that natural blood proteins like serum albumins can interact with different nanoparticles facilitating their penetration into the living cells. However, in the case of J-aggregates, albumins can destroy aggregates trapping separate cyanine dyes into their structure. Recently, we have found that one of the cyanine dyes, namely an amphiphilic derivative of pseudoisocyanine (amphi-PIC), forms J-aggregates which appeared to be more stable and efficiently emitting while interacting with bovine serum albumin (BSA) in buffer aqueous solution.

The aim of the study was to assess the stability of amphi-PIC J-aggregate in a complex with the blood components and to evaluate their toxicity in vitro.

To test the J-aggregate stability the blood of Wistar rats was used. The J-aggregates were prepared from a stock solution of amphi-PIC in DMSO by solving with serum, plasma, or blood at least 20 times and more. Similarly to the BSA buffer solution, the photostability of the J-aggregates appeared to be at least 3 times better compared with the buffer solution (when BSA was absent). In addition, luminescence intensity was increased as it was observed in the model experiment with BSA.

To test the J-aggregate toxicity, the 3–4 passages of primary cultures of rat embryonic fibroblasts were used. To exclude the DMSO toxicity, its effect on the cultures with no aggregates was studied as well. Cell shape, monolayer confluence, proliferation, membrane integrity, genotoxicity, migration, and metabolic activity, were evaluated. Summarizing the results, we can conclude that low toxicity was found at low dye concentration (10–5 M and less) and low DMSO content (2% and less), the most sensitive is the proliferative function of the cell.

Thereby amphi-PIC J-aggregate can be used in biological systems in low concentrations.

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Annealing Effect on Self-Trapped Exciton Radiation of Nanosized Y$_2$O$_3$ Ceramics Radioluminescence

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Yttrium oxide (Y$_2$O$_3$) has received considerable attention due to potential biomedical applications as high efficiency imaging formation, ceramics for prostheses, infrared converters into visible radiation in biomarkers, functional elements of ultrasensitive sensors, etc. [1]. The most experimental intentions have focused on the relationship between the luminescence properties and composition, structure of the Y$_2$O$_3$ phosphor, and especially the presence of dopants such as Eu$^+$ [2].

Our previous study demonstrated that X-ray induced luminescent radiation spectrum of nanosized Y$_2$O$_3$ ceramics included five spectral bands in the optical wavelength range [3]. Most wide band with maximum at approximately 350 nm was the peak associated with self-trapped exciton (STE) relaxation. The annealing effect of pellets pressed from this powder on STE radiation spectral characteristics was studied. Pellets were made from commercial Y$_2$O$_3$ nano- and micro-sized powder according to the technology described in detail in [3]. Some of the samples after sintering at atmospheric pressure at 1500°C temperature during 1 hour were additionally annealed at 1000°C for 10 hours.

The XRD and electron microscope studies did not reveal any significant changes in the crystallographic parameters as well as in the grain shape and size for the additionally annealed samples. At the same time, the luminescent spectrum study before and after annealing showed that there were changes in the STE peak. After annealing, the peak position and width changed but the shape was the same. The asymmetric shape of the peak is due to the fact that the energy of ground state as a function of configurational coordinate is represented by parabola curve. There was a shift of the short-wavelength and long-wavelength boundaries of the band, as well as the spectral maximum towards lower photon energies. It should be noted, the small shift was observed for the short-wavelength boundary and the larger for the long-wavelength one. Such relationship between shifts is explained by the corresponding change in the ground state energy. As a result, the peak width increased and the integral energy in the STE band decreased. Thus, the observed changes in the exciton radiation can be explained by an increase in the phonon frequency, on which the ground state energy depends [4].

Long-term irradiation of both additionally annealed and unannealed Y$_2$O$_3$ samples resulted in an exponential decrease in the STE band luminescent intensity. Such luminescence dynamics can be explained by the fact that part of the photoelectrons fell into the traps of grain boundaries, where relaxation occurs through a nonradiative mechanism. As the concentration of photoelectrons increased, the power of photoelectron source, which is directly responsible for the appearance of exciton d- and s-conduction electrons of yttrium and 2p-oxygen holes, decreased. As a result STE peak luminescent intensity decreased.

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Conference Track: “Nanobiomedical Research & Applications”
Influence of Carbon Nanoparticles on Human Sperm

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Improving the morphological and functional status of spermatozoa, which is important in the field of assisted reproductive technologies, can be achieved by using many physical factors. Most of pathologies are related to oxidative stress that manifests itself through LPO processes, oxidative modification of protein, damage of DNA and oxidative imbalance. Fullerenes are a molecular form of carbon, able to be powerful antioxidants and can be used in biomedicine. At the same time data are accumulating that their small size and very high surface per unit mass as well as significant reactive capacity allow them to penetrate biological barriers freely and to increase the production of reactive oxygen species, which causes damage to intracellular structures. The aim of this work was to investigate the peculiarities of the action of C60 fullerenes in concentrations of 10-40 μg/ml on the sperm cells.

Ejaculates from men with normozoospermia and asthenozoospermia (n = 10) were studied. C60 is a molecular-colloidal system of spherical fractal clusters, the structural unit of which is a highly hydrophilic complex. The size of the nano-compound is 1.6-1.8 nm. Motility, viability, morphological characteristics and chromatin state of spermatozoa were assessed. The integrity of the sperm membrane was assessed by staining with eosin-nigrosine and by flow cytometry on a FACS Calibur (Becton-Dickinson, USA) - 7AAD test.

Investigation of samples at normozoospermia and asthenozoospermia have shown that incubation with C60 at concentrations of 10 and 20 μg/ml for 1 hour increases the number of active-motility spermatozoa and does not lead to changes in the integrity of the head membrane in the case of normozoospermia and asthenozoospermia. Carbon nanoparticles at concentrations of 10-30 μg/ml had no significant effect on sperm viability in normozoospermia and asthenozoospermia. Activation effect of low concentrations can be associated with enhanced functional activity of mitochondria. Fullerene C60 is a powerful trap for radicals - its antioxidant properties are based on the electron deficiency of its molecules and the ease of attachment of free radicals. Fullerene derivatives act as traps for radicals in cells [1], prevent mitochondrial damage and DNA fragmentation without a toxic effect. The number of spermatozoa with condensed chromatin (7AAD+) at normozoospermia was 97.6%. Carbon nanoparticles in concentrations of 10 and 20 μg/ml does not cause changes in the vitality of sperm and the state of nuclear chromatin at normozoospermia and asthenozoospermia. However, at 30 and 40 μg/ml, there was a significant increase in the 7AAD+ sperm by 2.8 and 3.4% vs. control. Cytotoxic effect of fullerenes is manifested by increasing their concentration in the medium up to 30-40 μg/ml. Carbon nanoparticles in high concentrations added to the medium reduced the fertility potential of spermatozoa.

REFERENCES

Reactive Oxygen Species Scavenging by Small Gadolinium-Yttrium Orthovanadate Nanocrystals

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Abstract ID #NRA-0071

Oxidative stress induced by reactive oxygen species (hydrogen peroxide, superoxide anion, hydroxyl radical etc.) is the key factor in developing a variety of pathological conditions including diabetes, asthma, atherosclerosis, hypertension mellitus and cancer. To prevent or reduce the cell damages caused by reactive oxygen species, natural or synthetic molecules named antioxidants are commonly used. Recently, various inorganic nanomaterials, such as CeO2, Mn3O4, Co3O4 and Fe3O4 nanocrystals, have attracted growing interest as nano-antioxidants with reactive oxygen species regulating ability [1, 2].

Here, we report on high antioxidant behavior of small gadolinium-yttrium orthovanadate nanocrystals revealed by spectroscopic methods using various reactive oxygen species sensors, and propose the mechanism describing their reactive oxygen species scavenging action.

It has been found that in 2 nm gadolinium-yttrium orthovanadate nanocrystals more than 60% vanadium ions are presented in lower V4+ and V3+ oxidation states. Switching between V3+ ↔ V4+ and V4+ ↔ V5+ oxidation states allow gadolinium-yttrium orthovanadate nanocrystals to react with hydrogen peroxide (H2O2) and superoxide anion (O2•-) in enzyme-like manner and neutralize hydroxyl radical (•OH), and peroxyl radicals (ROO•), as well.

The obtained data and proposed mechanism of gadolinium-yttrium orthovanadate nanocrystals antioxidant action can explain the non-trivial anti-aging and radioprotective effects of gadolinium-yttrium orthovanadate nanocrystals observed earlier in vivo [3-5].

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REFERENCES

Synthesis, Structural Properties and Thermal Stability of Nanoscale Magnesium Whitlockite

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Magnesium whitlockite (Ca₁₁₂Mg₂H₂(PO₄)₁₄) is known as the second most abundant mineral in human body and one of the main components of human hard tissues, constituting to approximately 20-35 wt% [1]. This material is also well known for its excellent biological and osteogenic properties [2], therefore it is a promising candidate to be used as a bone regenerative material. However, research of whitlockite is limited and thorough studies of it are still important today.

In the present work, whitlockite powders were synthesised using hydrothermal synthesis method while using calcium hydrogen phosphate dihydrate and magnesium acetate tetrahydrate as starting materials. Synthesis was performed at a temperature of 160 °C for 3 h under hydrothermal conditions. Obtained powders were heated in different temperatures in a range of 400 to 1300 °C. After the heating process compounds were characterized using X-ray diffraction (XRD), Fourier-transform infrared spectrometry (FTIR), Raman spectroscopy and solid-state nuclear magnetic resonance (NMR). Scanning electron microscopy (SEM) was used to characterize the morphology of the particles.

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Optimization of the Extended Gate Field-Effect Transistor-Based Biosensing Platform for the Detection of Biomolecular Interactions

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Electrochemical biosensors are broadly applied to diverse diagnostic procedures, including many assays for the detection of therapeutic agents. Especially in theranostic applications, a controlled and cost-effective setting before entering the stage of in vivo trials is of crucial importance. However, to reach this goal, the performance of electrochemical biosensing platforms still should be improved in terms of stability and reliability. Multiplexing is a practical approach for improving biosensing performance by enabling simultaneous sensing of different analytes, accurate differential measurements, and robust measurement statistics. Biosensing devices based on field-effect transistors (FETs) are already widely used for electrical label-free detection of different biological and chemical analytes. Relying on the concept of the extended gate (EG) as an ultrasensitive and cost-effective sensing element, the EG electrode array can be integrated within a single chip while individual electrodes can be modified to target specific analytes or act as control sensing points. EG array coupled with a reusable FET transducer opens the possibility for multiplexed analyte sensing when supported with appropriate control and measurement electronics. Typical EG FET-based platforms do not focus on multiplexing and rely on external modules such as specialized instruments for electrical measurements.

We are developing a standalone multiplexed EG FET-based sensing platform with customized electronics enabling FET operation in constant charge mode for simplified signal readout and employing a common reference electrode for all measurement points. Interactions at the EG electrode surface are detected as a shift in voltage response between the source terminal of the FET and the reference electrode. Our platform aims to detect different analytes which are relevant for cancer theranostics such as cytokines, chimeric antigen receptor (CAR) T cells, and bispideine-based chelators used in positron emission tomography (PET) of cancer. Prerequisites for the emulation and detection of delicate biochemical interactions are careful optimization of the electrode surface functionalization process and stability of the voltage response between the extended gate and reference electrodes. Therefore, we present an optimization approach focusing on the pre-conditioning and functionalization of the EG gold electrode surface for the detection of biomolecular interactions also including the customized affordable reference electrode preparation for voltage response stability.

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Dendrimers as Gene Delivery System

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Dendrimers are radially symmetrical nanoparticles with a well-defined, homogeneous and monodisperse structure, in which we can distinguish: a symmetrical core, inner and outer shell with a large number of functional groups that are responsible for their high solubility and reactivity. Such a structure gives them valuable biological properties. Dendrimers have been widely studied as carriers of therapeutic agents, diagnostics, contrast agents, highly sensitive sensors, blood substitutes, and antibacterial and antiviral substances [1].

One of the most important potential applications of dendrimers is their use in gene therapy as carriers of nucleic acids, such as siRNA. Since siRNA is negatively charged, as is the surface of the cell membrane, it is being repelled and, on its own, is unable to penetrate the anionic cell membrane. Moreover, its effectiveness is limited due to its low enzymatic resistance. A promising tool for transporting nucleic acids are positively charged dendrimers. Cationic dendrimers are able to complex with nucleic acids via electrostatic interactions. The positively charged complexes intensify cellular uptake, therefore increasing the transport of therapeutics to cells [2, 3]. Transport of siRNA into the cell, makes it possible to selectively silence specific genes, and thus inhibit the progression of many diseases. [4].

The enormous advancement in better understanding the mechanisms responsible for selective gene silencing and the development of knowledge regarding how dendrimers can conjugate and deliver nucleic acids may make it possible to use gene therapy in the treatment of many diseases in the near future.

REFERENCES

Preparation and Characterization of Zinc-phosphate Based Nano-antimicrobial Coating for Smart Food Packaging Application

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Alarmingly, more and more infections are becoming resistant to antibiotics, which poses a great difficulty to treat infections. Unless we take action, we risk seeing a silent pandemic rising. On this note, scientific communities stand shoulder to shoulder to overcome the development of antimicrobial resistance so that still safe and available medicines can be used to treat infections. Development of nanoantimicrobials (NAMs) that inhibit or kill bacteria is an important topic and alternative strategy to fight against antimicrobial resistance [1, 2].

Zinc based nanoparticles (NPs) is already proven to exert antiviral and antibacterial activity [3, 4]. Compared to highly water soluble zinc salts and water insoluble ZnO, insoluble Zn phosphate (Zn3(PO4)2, Ksp = 9.0 x 10-33) could increase the rate of generation of biocidal Zn ions with improved stability and longtime antibiofilm activities. In the present study, synergistic Zinc-phosphate NPs with bioactive Quaternary ammonium compound (QAC) are produced via green and simple route, with the purpose that NAMs inhibit communities of pathogenic bacteria (biofilms) in smart food packaging system and in dental application. The influence of the synthetic parameters in the experimental condition brings novelty on the development of Zn phosphate NPs. Preliminary study suggests that Zinc-phosphate based nanocomposite could be beneficial against harmful bacteria provided that the activable Zn ion release could be implemented by pH changes of the medium. Characterization studies on the nanocomposite were done by Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), powder Xray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Infrared - attenuated total reflectance (IR-ATR) spectroscopic study is expected to monitor the real time in situ biofilms growth inhibition exerted by released Zn ions.

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REFERENCES

The Odd-Even Effect in Peptide SAMs – Competition of Secondary Structure and Molecule-Substrate Interaction

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Peptide-based Self-Assembled Monolayers (SAMs) are known to be crucial for the biocompatible surface on inorganic substrates applied for implants, biosensors or tissue engineering. Recently these bioinspired nanostructures have also been considered interesting for molecular electronics due to their surprisingly high conductance [1] and thickness independent capacitance [2] which make them promising for organic field-effect transistors (OFETs).

Our analysis incorporated the series of homooligopeptides based on glycine (Gly) with cysteine (Cys) Cys(Gly)\textsubscript{n}, \(n = 1\) - 9. Monolayers were deposited on both silver (Ag), and gold (Au) surfaces from a solution phase. Obtained monolayers show the secondary B-sheet structure formation, characteristic of proteins, as well as the odd-even structural effect, which affects packing density and conformation of molecules in the monolayer [3]. Results suggest that the origins of these structural effects may be related to either cooperative or competitive relation between the type of secondary structure formed by these molecules and the directional character of their chemical bonding to the metal substrate. The current analysis opens up the opportunity for the rational design of these biologically-inspired nanostructures, which is crucial both for mentioned biological and electronic applications.

REFERENCES

Ultra-small Palladium Nanoparticles – A Promising Tool to Enhance the Effect of Irradiating Cancer Cells with a High-Energy Proton Beam

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The increasing number of cancer cases requires finding newer and more effective methods of treating this disease [1]. One of the innovative strategies enhancing the effect of radiation-based anticancer therapies, is the use of metallic nanoradioenhancers, especially noble metal nanoparticles (Me NPs). Me NPs, added in a non-toxic concentration to the cell culture, may amplify the effect of their subsequent irradiation with a photon or proton beam thanks to physical (e.g. generation of secondary electrons, gamma rays etc.) or biological-chemical (e.g. creating reactive oxygen species, inhibition of the cell cycle, bystander effect etc.) mechanisms of radiosensitization [2-3].

Accordingly, ultra-small (ca. 3 nm), spherical palladium nanoparticles (Pd NPs) were synthesized. Physicochemical analyses of the obtained nanomaterials were performed using scanning transmission electron microscopy (STEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy and zeta potential measurements. In order to assess the interaction of Pd NPs with high-energy protons (225 MeV), generated by the Cyclotron Proteus C-235, charged-particle activation analysis (ChPAA) was also performed. Then, in vitro biological tests were carried out to evaluate the potential use of Pd NPs radiosensitizers. For this purpose, three colon cancer cell lines (SW480, SW620 and HCT116) with different aggressiveness and normal colon epithelium cell line (CRL-1790 – as control) were used. These cells were cultured with a non-toxic concentration Pd NPs and then irradiated by a proton beam (225 MeV, 15 Gy). The viability of cells subjected to this combination therapy was assessed by the MTS assay and annexin V-binding test. Moreover, the innovative 3D holotomographic microscopy (Nanolive 3D) technique was used to evaluate the dynamics of Pd NPs penetration into colon cancer and normal cells in real time.

The results of our research showed that ultra-small Pd NPs can be perfect tool to improve the effect of the irradiation cancer cells with proton beam. Importantly, this type of therapy caused only a slight decrease in the survival of normal cells, which is a prerequisite for their clinical application. It has also been shown that the biological-chemical, rather than physical mechanism of radiosensitization, is responsible for the promising effect of this therapy. Also from the economic point of view, the application of Pd NPs makes sense, because their production cost is much cheaper compared to more commonly studied so far, gold or platinum-based NPs [4] [5].

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Three-Dimensional Bioactive Surface Structure on Ti-based Implants

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Despite numerous technical solutions, appropriate host responses around the dental and orthopedics implants are still far from the ideal. The modified surface has to induce cellular responses that increase osteoinduction and osteoconduction [1]. Dental and prosthetic Ti-based materials require additional surface treatment for enhancing biological activity in dealing with implantation failures. Numerous surface modification methods have been described to accelerate osseointegration [2, 3]. However, studies demonstrate that the surface treatment protocols need to combine both physical and chemical processes. Therefore, we focused on developing new improved surfaces on Ti-based implants with structural characteristics that match enhanced mechanical, chemical and biomedical functional requirements. In particular, the implant surfaces have to provide structural support, guide cells towards healing and serve as a reservoir of ions for biochemical reactions vital to body homeostasis.

Hierarchical surface structure was fabricated on Ti implants by sandblasting followed by etching in oxalic acid and additional alkaline treatment. As a result, we achieved formation of developed surface structures at macro-, micro- and nano-levels. Accordingly, the macro- and micro-structures mimicked structural and physical characteristics of the host bone tissue. Importantly, the nano-level represented bio-inspired microenvironment to promote cell interaction.

Scanning electron microscopy (SEM), optical profilometry (both 2D, 3D) and tactile profilometry (2D profiles, 3D topography and roughness) have been employed to characterize the surfaces and prove their highly developed hierarchical topography. The SEM analysis showed that the surfaces had a rich hierarchical organization. Sandblasting formed the basic roughness. Acid etching resulted in bone-like surface morphology with pores and cavities amenable for cell adhesion and proliferation. The nano-level represented needle-like spines that densely covered the surfaces and further enriched the multi-level architecture of the surface.

Optical profilometry confirmed the results of SEM analysis. Sandblasting created dominant high and deep features on the surfaces (Sa (arithmetical mean height) = 1175 nm). These features remained in the same order of magnitude after the subsequent treatments. Acid etching increased (Sa = 1635nm) while alkaline treatment slightly decreased (Sa = 1119 nm) the value of Sa parameter previously achieved by sandblasting. Polishing resulted in smooth positively polarized surfaces (Sa=141 nm and Ssk(skewness) =6.48). Other treatments resulted in low Ssk values (sandblasted -0.11, etched -0.16, alkaline treatment -0.39) which indicates formation of neutral or negatively polarized surfaces.

In conclusion, our processing sequence and technological modifications offers rich multi-level architecture with unique functional characteristics which could enhance biomedical properties of Ti implants.

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REFERENCES

Ethical and Societal Aspects of Nanotechnology Applications in Medicine

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Abstract ID #NRA-0133

Nanotechnology implementation in the medical field improves health and increases life expectancy [1, 2]. However, today, only a small part of society is aware of modern advances in nanotechnology and can assess their benefits and risks. Medical students have professional knowledge in this field, so it is helpful to understand their ideas about ethical and social issues of nanomedicine.

This study aims to clarify the ethical and social aspects associated with the potential risks of using nanomaterials in various fields of medicine.

Methods: we used the focus group discussions method with Sumy State University medical students [3].

Results and discussion: The results showed that most respondents believed that the benefits of nanotechnology in medicine far outweigh the potential risks. The main factor that concerns students about the possible adverse effects of nanomaterials is the lack of information on the toxicological effects of nanoparticles and the long-term consequences of their introduction into the human body. On the one hand, nanocarriers can be used as effective systems for controlled delivery of drugs in the body and targeted therapy; on the other hand, they can trigger a humoral immune response in the body, which will perceive them as foreign elements. Due to their small size, nanoparticles are not subject to biotransformation, and they accumulate in the human body [4]. A question arises concerning the health of nanoindustry workers' protection and their awareness of the potential adverse effects of nanomaterials.

Another crucial ethical aspect is the feasibility of nanotechnology to make specific changes in the human body when there is no need for such changes from a medical perspective. An example of this is the application of nanomaterials in aesthetic medicine or for general health and to slow down the aging process [5]. In this regard, the question of social justice arises and the availability of nanotechnology to improve the physical condition of the human body. Low-income individuals do not have the opportunity to use modern advances in nanomedicine. The rapid development of nanotechnology has increased inequality risks between richer and poorer sections of the population and between countries that differ in the degree of economic growth.

Thus, nanomedicine's priority ethical and social issues include assessing the safety of nanomaterials and minimizing the potential risks to public health, which necessitates further research on the toxicological and pharmacological effects of various kinds of nanomaterials. Interdisciplinary discussions of risks are essential for nanomedicine to receive public support.

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Hybrid Plasmonic Nano-Architectures: Biokinetics and Potential Oncological Applications

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During the 90s, nanotechnology produced the first revolution in the clinical treatment of neoplasms through the release of Caelyx®/Doxil®, a liposome formulation of doxorubicin. Beyond the drug delivery enhancement associated with nanomaterials, noble metals are essential for the development of innovative or combined/enhanced non-invasive cancer treatments. However, no conclusion on the safety of inorganic nanomaterials has been drawn from the Scientific Committee on Consumer Safety (SCCS) nor from the Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) because of the lack of adequate biodistribution and safety data. In this scenario, it is of critical relevance to elucidate the fate of metal nanomaterials once administered to unlock their potentiality for patient care [1].

Here, the interactions of hybrid metal nanoparticles with living organisms will be presented. In order to evaluate the impact of the chemical nature of the nanomaterial on biokinetics, the ultrasmall-in-nano architectures (NAs) have been employed as a significant model to compare the bio/nano-interactions of noble metals [2, 3]. Furthermore, the critical impact on the biodistribution and clearance profile of the nanomaterial design, as well as the administration approach, will be discussed. Ultimately, the last achievements from the ultrasmall-in-nano architectures will be presented, and the next exciting perspectives will be provided [4, 5].

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Bionanomaterials: Design and Applications

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Abstract ID #NRA-0147

Nanostructure science and technology are a broad and interdisciplinary area of research and development that has been exponentially growing in the past few years. Engineered nanomaterials are resources designed at the molecular (nanometer) scale to take advantage of their small size and novel properties which are generally not seen in their conventional bulk counterparts. The two main reasons why nanomaterials can have different properties are: (i) the increase of relative surface area and (ii) the quantum confinement effects leading to novel optical, electrical and magnetic behaviors. In order to apply these nanomaterials in biofields and to increase the throughput of biobased nanostructured materials and devices for energy, environmental and health applications, an efficient immobilization of the biomolecules is needed by the control of the interfaces between the nanostructures and the immobilized biomaterials.

Here, we used different synthesis techniques such as atomic layer deposition (ALD), [1] electrospinning, [2] 3D printing, [3] and the exfoliation of Graphene and BN like Graphene etc. as the main tools for the creation of controlled nanostructured materials and interfaces in which the geometry can be tuned accurately and the dependence of the physical-chemical properties on the geometric parameters can be studied systematically in order to investigate their performances mainly in health applications. We will show examples of how these methods can be used to create: (i) optical and electrochemical biosensors [4] and (ii) bionanocomposites materials for tissue engineering in which the performance varies with the nanostructures/interfaces [5].

REFERENCES
Detonation Nanodiamond-Decorated Nitinol after Plasma Electrolytic Oxidation for Vascular Stent Development

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Abstract #NRA-0148

Improvement of stent materials and coatings has resulted in significantly low failure and re-interventions rate in coronary artery disease treatment [1]. But, despite of wide application of eluting stents technology, the late stent thrombosis is still severe complication in 3-5 years after the intervention due to degradation of eluting polymer coating [3]. We aimed to develop new coating technology via formation of functional plasma electrolytic oxidation layer doped with functionalized Detonation Nanodiamonds (DND). The functional surface groups of DND aimed to reduce cholesterol deposition due to van der Waals interactions and hydrogen bonding forces [3].

Concentrated H3PO4 (85%) was chosen as an electrolyte for Nitinol (NiTi) plasma electrolytic oxidation with current density 75 mA/cm² and voltage 50 V (NiTi-1), 60V (NiTi-2) and 70 V (NiTi-3). Structural properties of ceramic layer were assessed in Scanning electron microscopy (Hitachi S-3400N). All abovementioned PEO regimen provided formation of porous ceramic layer with increasing porosity with increasing applied voltage. Before the drop-casting of DND to the NiTi surface, cell toxicity of DND was evaluated in human fibroblast cell culture during 3 days experiment. PEO-treated surface decorated with DND (0.04 and 0.08 mg) using drop-casting technology. Fibroblasts were seeded to pure NiTi, PEO-coated and DND decorated surfaces to evaluate biocompatibility during the 7-day experiment.

Short term co-cultivation of DND with fibroblasts demonstrated high cytotoxicity in concentration over the 0.15 mg that consider as a maximum limit concentration for surface decoration. Long term experiment with fibroblast cultivation on NiTi samples demonstrate high biocompatibility of both polished NiTi surface, PEO-treated and DND-loaded samples. NiTi-2 regimen shown slightly less cell proliferation activity compare the control and the rest PEO samples. DND has ability for minor stimulation of cell proliferation on day 3 and do not exhibit any toxic effects up to Day 7. The NiTi-3 samples (70 V) demonstrated most favorable environment for cell attachment and proliferation within the 7-day period.

Our research demonstrates formation of porous stable ceramic layer on NiTi implants in concentrated H3PO4 solution and ability of DND application with lack of cell toxicity. This complex technology has potential for enhancing of vascular stent development technology.

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The Marriage of Atomically Precise Nanoclusters with Biomolecules: Interfacial Chemistry & Biological Applications

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Abstract #NRA-0152

Ligand protected metal nanoclusters (NCs) are an emerging class of quantum materials connecting the gap between atoms and bulk metallic materials [1]. Owing to their unique electrical, optical and other spectroscopic properties such as luminescence, they are very important in various applications such as sensing and bio-imaging. Concerning optical properties, strongly emissive nanoclusters are highly desirable. Strategies such as aggregation-induced emission, silver doping and ligand-shell rigidifying for increasing the photoluminescence (PL) quantum yield and tuning the PL colors of nanoclusters have been proposed. Nonlinear optical (NLO) characteristics of such quantum clusters have revealed remarkable features [2]. The two-photon absorption (TPA) cross section of ligated noble metal nanoclusters is several orders of magnitude larger than that of commercially-available dyes [3]. In this talk I will review promising applications of these fluorescent nanoclusters, with particular focus on their potential to impact the fields bio-imaging, and bio-labeling [4, 5]. Finally, scope for improvements and future perspectives of these novel nanomaterials will be highlighted [6].

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Periodic Surface Nanopatterns Can Determine Cellular Shape and Orientation

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Ultrashort lasers can be used to obtain specific nanopatterns called Laser Induced Periodic Surface Structures (LIPSS). They offer intriguing features for various fields, including biomedicine [1]. Thus, LIPSS can modify various surface properties, e.g. resistance to corrosion, hydrophobicity, and biocompatibility [2]. We aimed at investigating how linear well-ordered LIPSS nanostructures on the surface of flat specimens of steel grade 316L affect the attachment and proliferation of human umbilical cord mesenchymal stem cells (UCMSC). 1064 nm ultrashort EKSPLA Atlantic 5 ps laser was employed to create a uniform LIPSS (L$_{1064}$), while a 532 nm laser was used to obtain both a uniform pattern (L$_{532}$) and a grid of grooves with 40 µm spacing (LGv). A flat polished specimen (L0) served as a control. We preliminary found that the sample L$_{1064}$ demonstrated an increased ability to support cell proliferation. After cell culture experiments, we fixed the cells, obtained the scanning electron microscopy (SEM) images, and analyzed cell geometry and orientation in relation to the surface nanopatterns.

We noticed that cell shapes and orientations depended on the LIPSS patterns. Cells on the samples with particular LIPSS appeared to be more elongated compared to the control sample. We then aimed at quantifying the differences. For this, the SEM images were analyzed with ImageJ software to measure the geometric properties of the cells. All cells with clear visible borders were confined using hand drawing, and the geometrical properties of these cells were automatically measured. This way we determined maximum and minimum Feret diameters as well as Feret angles [3]. We also calculated the Aspect ratio (axial ratio, Heywood’s elongation ratio, 1946) – the ratio of maximum to minimum Feret diameter or vice versa [4]. Statistical analysis was performed using Graphpad Prism v.9.2.0 software.

First, normality test from the “Normality and lognormality” section was performed on the Aspect ratio parameter. Data from every sample passed each of four normality tests, allowing to use the t-test method. Then, we implemented a Student t-test to determine possible statistical differences between experimental groups and the control sample. The data showed that the L$_{1064}$ and L$_{532}$ samples were statistically different from the control sample (P-values were 0.0169 and 0.0005, respectively). However, we did not find similar difference between control L0 and gridded grooves LGv. Next, we analyzed the Feret angle distribution and dependence between the Feret angle and the angle of the LIPPS pattern. For this, we performed a Frequency distribution test with a step of 20 degrees to the Feret angle parameter. We found that each LIPSS sample except the control one showed a peak of the distribution of specific angles. Moreover, these peaks corresponded to the angles of the LIPSS patterns. We concluded that the cells grown on top of the LIPSS samples were oriented along the LIPSS pattern.

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The Effect of Silver Nanoparticles Against Formation of Enterococcus Faecalis Biofilms

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Abstract ID #NRA-0167

The main factor of bacteria pathogenicity is the ability to organize biofilm, that increases the resistance of microorganisms to antibacterial agents. Nanomaterials are promising substances with antimicrobial activity due to its unique physicochemical properties such as ultra-small sizes, large surface-area-to-mass ratio, and increased chemical reactivity [1]. The aim of this study was to evaluate the antibacterial efficacy of silver nanoparticles (AgNPs) against Enterococcus faecalis that could causes severe infections due to naturally resistant to most antibiotics. And taking into account possible biofilm formation, eradication of Enterococcus faecalis posses serious medical challenges [2].

AgNPs were obtained by chemical method with PVP as a reducing agent in cooperation with NanoWave (Poland) [3]. Antibacterial properties were examined with determination of the Minimum inhibitory concentration (MIC), and Minimum bactericidal concentration (MBC). The influence of AgNPs on biofilm formation evaluated by detection of the biofilm mass inhibition (with gentians violet assay) and determination of the AgNPs’ effect to the biofilm ultrastructure with Scanning Electron Microscopy.

AgNPs demonstrated appropriate antibacterial properties with inhibition of bacterial growth in concentrations of 5 μg/ml (MIC) and kill bacteria in concentration of 10 μg/ml (MBC). It should be noted that AgNPs do not affect bacteria attachment in these concentrations. Increasing of concentrations up to 40 μg/ml lead to decreasing of biomass quantity in Day 1 and Day 2 of biofilm formation circle compared to the control. We did not find the changes in biomass quantity in Day 5, but notice the structural changes in bacteria cell wall.

We demonstrated that AgNPs can be used for effective treatment and prevention of infections caused by Enterococcus faecalis in concentrations ranges from 10 to 40 μg/ml.

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Biocompatibility of the Materials with Laser Induced Periodic Surface Structure

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Laser induced periodic surface structuring (LIPSS) is an arrangement of (quasi) periodic topographic lines representing a linear surface grating structure [1]. It is caused by the irradiation of a surface with linearly polarized, pulsed ultra-short laser that allows generation of well-ordered nanostructures with periodicities in the order of the utilized laser wavelength [2]. These nanosized patterns imitate the surface morphologies found in nature and can stimulate cell adhesion and proliferation [3-5]. Consequently, LIPSS technology could make substantial progress in producing enhanced cardiovascular stents or bone implants. Because of a great variety of possible patterns, alloys for a material base and laser parameters, it is still unclear which combination would match better for the tasks at hand. This project aimed at investigating interaction of the cells with patterned biomaterials to determine the level of biocompatibility of LIPSS obtained by various laser wavelengths.

Steel grade 316L was chosen as a base for laser structuring due to previously reported ability to promote adhesion, proliferation and migration of human umbilical vein endothelial cells [4]. 1064 nm wavelength beamlines were employed to create a uniform distribution of LIPSS (L1064), while 532 nm wavelength created both uniform (L532) and a structure in the form of 40 µm grid of grooves (LGV). Untreated polished samples (LO) as a control. Human umbilical cord mesenchymal stem cells (UCMSC) at a density of 10000 cells/cm$^2$ were grown in 24-well cell culture plates on top of the LIPSS samples in DMEM/F12 medium with the standard amount of antibiotics and 10% foetal bovine serum. Wells containing only medium served as the negative controls. Cell adhesion and proliferation rates were assessed by resazurin reduction assay on the 1st, 2nd, and 3d days post plating.

On the 1st and 2nd days there was no significant difference between the polished and LIPSS groups (Fig. 1) indicating that the materials did not show any cytotoxicity and enabled the cells to attach to the surfaces. However, on day 3 a higher rate of resazurin reduction was observed on the sample L1064 compared to L532. The polished control LO and grooved sample LGV also showed a trend to differ from the L1064, but they did not reach statistical significance. This indicated that the uniform structure L1064 served as a better surface for cell proliferation. To summarize, nanopatterns created by LIPSS can successfully stimulate attachment and proliferation of mesenchymal stem cells and can be promising for the development of next-generation implants.

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Conference Track: “Nanobiomedical Research & Applications”

11nra-31
Novel Transdermal Liquid Crystal System for Drug Delivery Enhancement

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Nanobiomaterials seem to be promising for various applications, including drug administration. As it was shown in [1], liquid crystal (LC) systems based on cholesterol esters can be used as efficient enhancers of skin permeability [2]. In this work, a novel LC system, which is a mixture of cholesterol esters (cholesteryl pelargonate, valerate, and succinate), was used as a matrix for deposition and transdermal delivery of various pharmaceuticals. The LC systems were loaded with 5 % w/w of monocyclic terpenoids (menthone, carvone, verbenone or camphora) as potential anticonvulsant and anti-inflammatory agents [3].

Properties of the LC systems were studied using optical microscopy (OM), differential scanning calorimetry (DSC), as well as spectroscopy of selective transmission (SST), which is a specific method for characterizing cholesteric LC systems [4].

SST studies were carried out using Shimadzu UV-2450 spectrophotometer. By means of SST technique, the neat (unloaded) LC system was shown to possess cholesteric helical twisting. For the neat LC system, the wavelength of minimum of selective light transmission (reflecting the cholesteric helical pitch) falls into the range of 380 to 650 nm depending on temperature. In particular, under skin temperature (30 to 36 °C) this range is 490 to 570 nm, which correspond to ‘blue to green’ color of the system. Loading with the terpenoids non-specifically disturbs the range of the LC helical pitch. It becomes narrower and shifts to the shortwave region, 410 to 450 nm, which correspond to ‘violet to blue’ color at the skin temperature.

DSC data were collected using Mettler DSC 1 microcalorimeter. They allow us to identify temperature ranges of the cholesteric mesophase existence in both neat and loaded LC systems. It was established that this range covers the temperature of ~40 °C for all the systems, but its limits could be downshifted significantly (by 10 to 25 °C) depending on the drug structure. Data of repeated thermal scans suggest strong binding of the terpenoids with the LC matrix providing their reliable deposition.

OM data were in line with SST and DSC results and confirm the occurrence of reversible temperature-driven phase transitions smectic – cholesteric – isotropic (liquid).

Thus, it can be concluded that the proposed novel LC systems loaded with monocyclic terpenoids retain their nano-scale helical structure at skin temperature and therefore could be further used as perspective systems for transdermal drug delivery.

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Development of Nanocomposite Antimicrobial Polymeric Materials Containing Silver Nanoparticles

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The presence of antibacterial materials in biomedicine and related fields of science and technology has become essential. Among the functions more desirable for materials used in medicine antibacterial action occupies one of the first positions, because bacterial growth could be prevented on medical devices, prosthetic materials, catheters (urinary or venous catheters) and surgical masks. Silver nanoparticles have high surface area, high active surface and represent a reasonable alternative for boosting the development of new bactericides. Excellent antibacterial activity and low cytotoxic potential of silver nanoparticles generally depend not only on their size, but also on the distribution in matrix media. The development of stabilized polymer-silver nanocomposites containing nanoparticles is considered to be one of the most promising solutions. Here we show the novel aproach for synthesis of stabilized silver nanoparticles and study of functional properties of antimicrobial polymeric nanocomposite materials based on polyethylene oxide. Using the novel aproach for synthesis we recieve silver nanoparticles with average size around 8-10 nm. We found that stabilized silver nanoparticles has a significant effect on thermophysical and dielectric properties of polymer matrix at relatively low concentrations of the nanofiller (~ 1-2%). Nanocomposite with 1 % of silver nanoparticles shows significant activity for Klebsiella (zone of inhibition is 19 mm) and material with 2 % of silver nanoparticles shows significant activity for Staphylococcus aureus (zone of inhibition is 22 mm). Our results demonstrate that synthesized stabilized nanoparticles have low tendency to aggregation in polymer matrix. We have developed new materials with high antimicrobial activity and improved physical properties. The novel aproach for synthesis of stabilized silver nanoparticles open a new window of possibilities in the development of new antimicrobial materials, based on various polymer matrix: from thermoplastic to elastic. The developed materials with improved functional characteristics in the future can be used as antimicrobial coatings, antimicrobial films and creams, as well as construction products with the necessary functional characteristics and antimicrobial function.

REFERENCES

Towards Water-Soluble Fullerene Nanomaterials for Pancreatic Cancer Treatment

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Pancreatic ductal adenocarcinoma (PDAC) is an extremely aggressive type of cancer with a poor prognosis and a five-year survival rate of less than 5%. Unfortunately, traditional chemotherapy, which is usually based on gemcitabine is not effective. Although new therapies are vigorously sought after in this field, no efficient remedy is available as yet, including novel drug design strategies, such as nanomedicine, immuno-, or gene-related therapies[1]. The main goal of our studies was to develop [60]fullerene-based nanoprotocols for the treatment and diagnosis of pancreatic tumors. The first line of chemotherapeutic drugs that were used to treat pancreatic cancer was gemcitabine and EGFR kinase inhibitor Erlotinib.

We divided the study into two parts- firstly we focused on the synthesis of C60-gemcitabine(nanoC60GEM) conjugate via Bingel Hirsch reaction [2]. The developed synthetic protocol was able to produce a highly water-soluble[60]fullerene nanoconjugate with gemcitabine in good yields. The physio-chemical characteristics of the fullerene nanomaterial confirm that two gemcitabine units are attached to the [60] fullerene scaffold via the formation of amide bonds. In the second approach, we synthesized the triazole derivative of erlotinib, which was further conjugated with gadolinium containing aminofullerene Gd@C82. We characterized modified buckyballs using NMR, FT-IR, UV-VIS, and XPS spectroscopy; each step of synthesis was also monitored using ESI and MALDI mass spectrometry. The size and morphology of synthesized fullerene nanomaterials were analyzed using dynamic light scattering methodology followed by TEM analysis, confirming the formation of fullerene aggregates. For gadolinium containing fullerene derivative Gd@C82, both relaxation times T1 and T2 were measured, confirming its high potential for use as an MRI-contrast agent. For all synthesized fullerene nanomaterials photochemical studies (singlet oxygen phosphorescence and EPR-spin trapping) were also carried out to measure the generation of singlet oxygen and superoxide.

All tested fullerene nanomaterials were tested for their cytotoxicity effects on pancreatic cancer cell lines (Pan-01, PAN-02, and AsPC-1) studying in-depth their cellular mechanisms of action, in particular cell death, cell cycle, and autophagy.

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The Kinetic of Silver Ions Release from Hydroxyapatite-AgNPs

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Hydroxyapatite (HA) has been widely used as an implant material due to its high chemical similarity with the mineral component of bone extracellular matrix. Silver nanoparticles (AgNPs) effectively used for treatment of bacterial infection in different localizations [1]. Bone infection, special after implantation and surgery procedures required application of topical antibacterial materials and HA with silver nanoparticles could be an effective way to prevent bacterial infection [2].

In this work, HA powders were synthesized by three different types of synthesis due to chemical precipitation in aqueous solutions. Sample 1 - non-stoichiometric calcium deficient HA; samples 2 and 3 – stoichiometric HA synthesized by two different ways. The sorption capacity of various types of HA was measured. The aim of current research was the assessment of silver ion release and sorption/desorption kinetic from different kinds of HA that used for bone grafting.

Concentration of AgNPs in the initial solution was 18.625 μg/mL. HA samples (as prepared suspension) were mixed with AgNPs solution in relation 1:1 for 72 hours at 25°C. The ability of HA to decrease the release of Ag+ ions from AgNPs due to adsorption was investigated at three kinds of hydroxyapatites differs by relation of components and types of synthesis. We estimate the influence of ultrasound on silver release. The obtained suspension was kept for 30 min in an ultrasonic bath (40 Hz) with following centrifugation at 8000 rpm (10 min). The concentration of Ag+ ions in supernatant solution was measured by the atomic absorption spectroscopy method (AAS) using S-115 M1 spectrophotometer. The highest Ag+ ion release ability was observed for calcium deficient apatite that could be explained due to the vacancies in Ca-deficient apatite crystal structure. The highest amount of released Ag+ ions was 1.2-1.3 μg/mL.

AgNPs and Ag+ ions have traditionally noted to have antimicrobial and bactericidal properties [3]. We studied antibacterial properties for different concentrations of AgNPs in HA 5,10,20,50,100,200 μg/mL. Suspensions were placed in thermostat overnight at 37°C. Then 10 mL of suspensions were placed on filter paper and dried at room temperature. Bacterial suspensions 105 CFU/ml were inoculated on plates with nutrient agar (for staphylococcus – nutrient agar, for enterococcus - enterococcal agar) and dried for 1 hour. Previously prepared discs were placed on agar and incubated for 24 h at 37°C. The result was evaluated by measuring the zone of bacterial growth inhibition. There is a growth inhibition of 1 mm, which confirms the contact inhibition of silver nanoparticles with minor possibility to cause deep release the ion in the media at MIC concentration. A broader perspective for this investigation is to obtain HA based materials with controlled concentration of AgNPs and predictable amount Ag+ ions release. Due to these prolonged action of obtained composites will be provided.

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Analysis of Amoxicillin Stability in Polymers Used for Formation of Antibacterial Coatings on Titanium Implants

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Titanium implants such as bone wedges, dental implants, and various bone plates are widely used in veterinary. The fast osseointegration process is one of the requirements for novel biomaterials dedicated to bone tissue. Integration of the implant with bone decreases the possibility of septic inflammation; thus, their surfaces are modified.

The anodization process is one technique that allows forming a porous oxide layer on complicated shapes of titanium implants. The titanium oxide layer could be enriched in bioactive or antibacterial chemical compounds from anodizing bath [1, 2]. However, the incorporation of selected antibiotics in the oxide layer is not possible due to their sensitivity to spark discharges during plasma electrolytic oxidation. Instead, the porous oxide layer formed on the dental implant could be covered by a polymer, e.g., poly(sebacic anhydride) or poly(lactide-co-glycolide) with amoxicillin. This antibiotic is used to treat bacterial infections, including dental abscesses. Microbiology analysis showed that the concentration of drug released from the proposed hybrid coatings is enough to decrease gram-positive bacteria activity such as Staphylococcus aureus ATCC 25923 and Staphylococcus epidermidis ATCC 12228.

The stability of the drugs on the implant surface is essential for their suitability for use. Our previous work [3] showed that the stability of amoxicillin decreased in a water-based solution. This work presents the analysis of amoxicillin stability in polymers such as poly(sebacic anhydride) PSBA and poly(lactide-co-glycolide) PLGA. The preliminary concentration of amoxicillin was 25 µg/mL in 1% solution of the polymer. The samples were dried to obtain a polymer foil and stored under various conditions (room temperature, fridge, freezer, and incubator with controlled temperature: 37°C). Analysis of drug concentration in polymers was carried out every day (up to 5 days) using high-performance liquid chromatography. Analysis was provided for three independent series with triple repetition and two injections per sample. Results indicated that room temperature did not significantly influence amoxicillin stability in these two polymers up to two days of storage (preliminary content between 91% and 97%). After four days, the stability of amoxicillin decreased in PLGA to 71% average preliminary content. In PSBA polymer, the amoxicillin showed better stability, no lower than 91%. The samples stored in the fridge and freezer showed that the content of amoxicillin was similar, not depending on the type of polymer, but decreased by around 12%. Storage of the polymers in the incubator caused the preliminary content of amoxicillin to decrease, but no lower than 18% for PLGA and 22% for PSBA. No additional signals coming from the degradation product of amoxicillin were registered on the chromatogram.

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Rheological Properties of Aqueous Suspensions of Hemostatic Composites Based on Nanosilica and Sodium Alginate in the Presence of Gelatin Protein

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The development of modern hemostatic agents with high efficiency is extremely relevant today during hostilities, but even in peaceful life, such materials are in demand to prevent severe blood loss caused by injuries [1]. The basis for the synthesis of such hemostatic materials in this work was a hybrid organo-inorganic nanocomposites (NC) based on nanosilica, modified with sodium alginate (AlgNa) in an amount of from 5 to 20 wt.% (per content of SiO$_2$). The developed NC showed high hemostatic properties in the case of parenchymal bleeding from rat liver in relation to the main parameters of hemostasis, namely the time of cessation of bleeding and blood loss. To determine the mechanisms of hemostatic action and predict NCs interaction with blood components, it is important to study the adsorption of proteins on the surface of the developed NCs. In this work, the adsorption of gelatin as a model protein on NC synthesized with different ratios of components (nanosilica/AlgNa) was investigated and the effect of this adsorption on the rheological properties of the aqueous suspension of the obtained powder samples was determined.

Analysis of the obtained data indicates that such suspensions have thixotropic properties and are characterized by a rheological curve with decreasing viscosity with increasing shear rate. It is shown that in aqueous suspensions with a solid phase concentration (composite) of 5 wt. % without the addition of gelatin, there is a monotonic increase in the effective viscosity of suspensions with increasing AlgNa content in the NC. Thus, the lowest Bingham viscosity (practically undestroyed structure) for 5 % wt. of the nanosilica suspension is 14.8 mPa·s (at shear rate 9 s$^{-1}$), and for the composite suspension with AlgNa content of 20 wt.% is 360 mPa·s. In general, the viscosity of structured dispersions is dependent on the dispersion medium viscosity and the interparticle interaction, which can be realized as a mechanism for bridge macromolecules bonding with different dispersed phase particles in the systems containing proteins. In the case of adding gelatin to aqueous suspensions of the NC, there is an extreme dependence of the viscosity of such suspensions with a maximum at low AlgNa content in the NC. Thus, the composite with 5 wt. AlgNa show the highest value of effective viscosity (1000 mPa·s) of aqueous suspension, which can be explained by greater gelatin adsorption on their surface and consequent formation of bridging macromolecular bonds between composite particles in aqueous suspension. Decrease in viscosity of suspensions of samples with 10 and 15 wt. % of AlgNa (300 and 240 mPa·s, respectively) correlates with a decrease in gelatin adsorption due to the shielding of the surface active centers of nanosilica (silanol groups) by the AlgNa for ability of interaction with gelatin functional groups.

REFERENCES

Thermosensitive Hydrogel Nanocomposites Based on N-Isopropylacrylamide and Acid-Activated Laponite®RD: Tunable Release of Doxorubicin

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Smart pH- and thermosensitive hydrogels are promising materials to design controlled drug release systems, which can provide reducing off-target side effects in cancer treatment. Hydrogels based on N-isopropylacrylamide (NIPAAm) are of high interest due to their temperature of the phase transition from the swollen to collapsed state (32 °C). This means that the material would release the drug at a temperature close to body temperature. One of the ways to improve the mechanical and functional properties of hydrogels is through physical cross-linking by clay materials (compared to traditional chemically cross-linked hydrogels) [1, 2]. We used nanosized synthetic clay Laponite (Lap) in pristine and acid-activated forms for the synthesis of NIPAAm-based hybrid organic-inorganic nanocomposites. This work aimed to study the release of the anticancer drug doxorubicin from thermosensitive hydrogel matrices based on N-isopropylacrylamide and acid-activated Lap (aLap) at different temperatures and pH values.

The acid activation of Lap was carried out using 1 N, 2 N, and 8 N sulfuric acid solutions by stirring at 70 °C for 2 h. The synthesis of physically cross-linked hydrogels based on Lap and aLap was carried out in an aqueous medium at 35 °C using the redox initiating system “Potassium persulfate - N,N,N’,N’-Tetramethylethylenediamine”.

It has been established that the temperature of phase transition from swollen to collapsed state for the obtained thermosensitive hydrogels is 31–32 °C and its intensity increases (almost by an order of magnitude) with an increase in the degree of acid activation of the initial Lap. The release properties of the synthesized physically cross-linked thermosensitive hydrogel nanocomposites were also studied. In particular, using immobilized cytostatic doxorubicin, it was shown that the release of the drug is significantly (1.5–3 times) intensified when heated (in the physiologically acceptable range from 32 to 45 °C) and when the pH changed from neutral to slightly acidic (characteristic of the affected tissues). The degree of acidic activation of Lap also influences the release properties of the nanocomposites: upon transition from pristine Lap to an aLap treated with an 8 N solution of sulfuric acid, the degree of release of the anticancer drug increases from 20–40 % to 80–90 % (depending on pH and temperature).

Synthesized physically cross-linked thermosensitive hydrogel nanocomposites seem to be extremely promising for the creation of modern drug carriers (in particular, anticancer drugs) with their targeted transport to the target organ and subsequent controlled release.

REFERENCES


Fumed Silica – Matrix Nanobiocomposite of Curcumin in Various Tautomeric Forms

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The plant polyphenol curcumin (Cur) has anti-inflammatory, antioxidant, neuroprotective, hepatoprotective and other properties. Its pharmacological activity largely depends on the ratio of its ketone (Cur-K) and enol (Cur-E) tautomeric forms, so understanding the dynamics of Cur tautomerization is fundamental in the development of drugs, dietary supplements and for predicting clinical reactions.

The purpose of this work was complex quantum-chemical, sorption and spectral studies of the curcumin keto-enol tautomerism in the process of preparation of its nanobiocomposites with fumed silica (trademarks “Atoxil”, “Polysorb”) by the adsorption from water-ethanol solutions used in technology to increase the bioavailability of poorly soluble drugs.

It was found that keto-enol tautomerism of Cur is observed in water-ethanol solutions. Cur-E exists at ethanol concentrations >50%, and with water addition the tautomeric equilibrium shifts towards Cur-K. Quantum-chemical calculations (solvation model SM 5.42 / 6-31G (d), GAMESSPLUS) of various curcumin isomers confirmed that in aqueous solution existence of Cur-K is more thermodynamically favorable. The ratio of ketone and enol forms depends also on the permittivity of water-ethanol solutions: at $\varepsilon < 45$, curcumin exists only as Cur-E when at $\varepsilon > 45$ the relative amount of Cur-K increases proportionally to the solution permittivity.

Curcumin tautomers adsorb on silica in different ways. At low curcumin concentrations in solution (<1.5\times10^{-4} M), a monolayer on the sorbent surface is formed only by the adsorption of Cur-E, apparently due to its linear structure. Non planar Cur-K begins to adsorb only at Cur concentration > 1.5\times10^{-4} M as part of molecular assemblies – aggregates with coplanar geometry, which are formed in curcumin solutions.

The found patterns make it possible to develop practical recommendations for the preparation and standardization of nanocomposites based on silica and Cur.
Discovering in Vivo Host Response to Nanomaterials

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Over the last decades, nanomaterials (NM) have been widely applied in medicine, facilitating tissue engineering, diagnostic technologies development, tumor treatment, drug and gene delivery [1, 2]. However, the opposite side of NM in vivo application is their integration and interplay with host cells and tissues. The host response is the core determinant of clinical efficiency and successful NM application [2, 3].

NM-host cell cross-talks and proper NM functioning in vivo depend on both biomaterial properties and the host response. A wide range of NM-related factors includes composition, size, shape, mechanical properties, coating, surface topography, and molecular landscape [2, 4]. From the opposite side, host reaction is complex and defined by local and systemic factors. At the organism level, age, diet, and metabolic parameters, various pathologies and their complications can affect NM-host interplay [5]. Besides, the intervention site, tissue-specific barriers, cellular content, metabolic, molecular, and even microbial landscape can modulate NM integration, functioning, and performance [1, 5].

Assessing host reaction to NM application needs distinguishing between tissue reaction on intervention and specific response to NM effects. The type of tissue and cells affected matters as various tissues differ in vascularization, cell-matrix balance, metabolic activity, and signaling pathways [4]. Considering the nanoscale of biomaterials used for nanomedicine, understanding the molecular interactions between NM and host cells of various lines and under dynamic conditions is essential [3, 5].

Safe and efficient NM development for further clinical application dictates the need for appropriate preclinical investigations with corresponding study design, methods, and biomarkers for assessing biological response with respect to expected NM effects and targets.

REFERENCES

Prevention of Biomaterial-Centered Infections by Nanoscale Surface Functionalization

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The challenges of biomaterials surface engineering are to introduce specific properties which result in optimization of the material-tissue interface. As far as polymeric materials are concerned, the most explored surface functionalization method is plasma. Such treatment results in the synergistic effect of physical (nanotopography) and chemical (surface groups) modifications and allow to obtain biocompatible and bacteria-resistant surfaces for novel, functional implants.

Surfaces can be called antibacterial when the attachment of bacteria is hampered due to their physical or chemical morphologies or compositions. Bacterial adhesion to surfaces is strongly affected by the surface properties and the bacterial cell wall. Because of the cell wall, bacteria are significantly less deformable therefore, bacterial sensitivity to surface topography is limited to irregularities smaller than their dimensions, i.e. various surface topographies result in dramatically different bacterial surface colonization. The study aimed to use AFM, XPS, SIMS, and biological tests and provide the basis for a better understanding of the complex interplay between biomaterial surface properties and early steps of infection.

We examined the unmodified and plasma-modified semicrystalline (parylene C) and amorphous (polyurethane) polymeric films in terms of surface properties, bacteria adhesion, and ability to form biofilm. S. aureus, S. epidermidis, P. aeruginosa and E. coli strains were used for the studies. The obtained surface-functional groups were characterized using XPS and SIMS, and changes in surface topography were followed with AFM and SEM observations. Selected samples with various topographies (smooth - nanorough - microrough) were used in microbiological tests.

It was revealed that the adhesion rate of S. aureus to modified and plasma-treated parylene C was within experimental error. Similar observations were made for P. aeruginosa. To gain better insight into the biofilm formation ability on the examined surfaces, SEM observations were performed. It was revealed that although the number of adherent bacteria cells can be similar between investigated samples, the nature of adhesion can vary. Early-stage biofilm formation occurred significantly faster on smooth polymeric films than on nanorough. The results of these investigations are significant from a clinical perspective, as delaying the onset of biofilm formation has significant benefits, particularly for implantable biomaterials; most antibiotics cannot penetrate through biofilms to effectively kill bacteria and therefore become ineffective.

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Edible Sensor for Electric Impedance Spectroscopic Analysis of Bioactive Liquids Containing Silver Nanoparticles

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In recent years, nanotechnology has attracted a lot of attention in dentistry and biomedicine, with new methods for oral and general disease prevention and treatment emerging. Formulations of silver nanoparticles (AgNPs) with antimicrobial properties against a wide range of microorganisms are one of these methods [1]. Since ancient times, the antibacterial effect of silver on various microorganisms has been well documented. Silver is typically used to cause antimicrobial effects in the form of nitrates, but when silver nanoparticles (AgNPs) are used, the surface area available for microbe exposure is increased. Toxicity concerning AgNPs in laboratory studies has garnered different results, depending on particles’ size, concentration, surface, and charge. Concerning oral and maxillofacial applications, their use is worth paying attention to, as it was not thoroughly investigated [2, 3]. Biodegradable electronics, also known as green electronics, is a novel concept that involves electronic devices that can naturally degrade or dissolve into the environment. Electronic devices have the potential to provide promising solutions for continuous monitoring of physiological parameters in humans [4].

The aim of this study was to evaluate the possibility of detection and electrochemical characterization of two commercial solutions with 15 and 30 ppm silver nanoparticles using edible sensors with gold electrodes using electric impedance spectroscopy. For this research, sensors were made of edible materials (gold electrodes on protein base). The EIS measurements were performed with PalmSens4. The three-electrode design with counter (CE), reference (RE) and working (WE) electrode was used. The impedance was measured in the frequency range from 1 Hz to 200 kHz. Firstly, a dry platform (dry sensor) was applied without delivering any solution, followed by the application of deionized water, 15 ppm and 30 ppm solutions to detect differences in the modulus of impedance. A function of an impedance modulus and phase angle were measured. The results speak in favor of sensitivity, consistency and applicability within the experimental sensing system on the tested sensors. It was shown that characteristic EIS signals were observed in both tested liquids, with a pronounced characteristic decrease in the impedance value corresponding to the concentrations of silver nanoparticles. As a proof of concept, the proposed structure successfully differentiated two types of tested solutions by measuring the decrease in impedance compared to the dry edible sensor and deionized water. Increasing the concentration of AgNPs resulted in decreasing the measured modulus of impedance. The presented platform could be very useful for applications where edible electronics and nanoparticle-containing solutions should be combined, such as the controlled release of AgNPs for medical applications, as well as the measuring of the therapeutical concentrations.

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Conference Track: “Nanobiomedical Research & Applications”
Carbon Fibers Surface with Active Metallic Nanometric Layer to Support Cartilage Regeneration Process

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Low-modulus carbon fibers (CF) are a material known in medicine due to their high biocompatibility [1] and a biomimetic character (extracellular matrix of cartilage tissue) [2]. A carbon nonwoven fabric with a controlled fiber diameter and defined surface can stimulate the process of regeneration of cartilage tissue damage [3]. However, the process is difficult to support and monitor. Thus, in the study we present carbon fibers with an iron (Fe) layer that was applied to monitor the behavior of the nonwoven fabric in the body by magnetic resonance imaging (MRI). Preliminary nuclear magnetic resonance (NMR) behavior of water saturated nonwovens was examined. In the research, a polymer precursor made of polyacrylonitrile (Zoltek Hungary) was used, which was then given a two-stage thermal conversion: oxidation (240°C/30 min) and carbonization in a protective atmosphere (970°C/5 min). Magnetron sputtering used an iron target (Leica, GB) and was applied in short bursts for 2 min (called CF/Fe2). At the end, CF/Fe2 fibers were additionally marked with the time of vapor deposition. Fiber morphology changes were observed under a scanning microscope (Nova NanoSEM, FEI). The study of the surface of CF and CF/Fe2 was carried out on a Raman spectrometer (inVia, Renishaw) with a lens with a magnification of 50 (excitation laser wavelengths: 785, 514.5, 442 nm). The BET method was used in the study of the structure of the nonwovens. NMR longitudinal (T1) (repetition time, TR=10 s, minimum/maximum π/2 pulse delay, τmin/τmax=0.05/12 500 ms) and transverse (T2) (echo time, TE=0.4 ms, number of echoes, NoE=50000, TR=4350 ms) relaxation times were measured on 2 MHz Magritek Rock Core Analyzer (Aachen, Germany) by using Inversion Recovery and Carr-Purcell-Meiboom-Gill pulse sequences, respectively. Iron aids cell culture viability, making this material attractive for biomedical applications and further NMR research [4, 5]. SEM images indicate that the Fe layer had 4 nm and deposition of iron from the vapor phase causes structural defects on the fiber surface. Based on the ratio of intensities from 1350 and 1590 cm−1 wavelengths, Fe deposition causes increase of CF fibers organization. Overfilled samples showed NMR differences. For CF/Fe2 fibers, pore-associated component has lower T1 (-25%) and T2 (-13%) values resulting from stronger interactions of water on the Fe-rich surface. CF/Fe2 had additional T2 component with higher than CF T2 time. This component is almost invisible for CF especially in T1-T2 correlation experiment. The origin of this component for CF/Fe2 needs further attention, since it is not correlated with the decreased lumen of interfiber space as confirmed by BET (SBET for CF/(CF/Fe2): 6.7/4.5 m2/g). More information on the strength of surface interactions in the Fe-coated nonwovens are inferred from decreasing saturation experiments.

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Nasal Immunization Using Chitosan Nanoparticles with Glycoprotein B of Murine Cytomegalovirus

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The nasal route of vaccination represents a novel and perspective alternative to more conventional parenteral injection. Moreover, mucosal delivery of antigens can induce both humoral and cellular immune responses. However, there are still some limitations such as rapid mucociliary clearance, poor immunogenic response and enzymatic barrier [1]. These obstacles can be overcome by the incorporation of the suitable adjuvants and the application of nanoparticles as the mucosal vaccine delivery system. The use of chitosan nanoparticles (ChiNP) as delivery system for a specific antigen offers advantages including biocompatibility, low toxicity and sustained release of loaded antigen [2]. In this study we tested the ability of nasally administered chitosan nanoparticles loaded with glycoprotein B (gB) of murine cytomegalovirus to induce immune response in Balb/c mice animal model. Balb/c mice were intranasally immunized by the three-dose protocol with ChiNP+gB, ChiNP+gB+adjuvants, gB and PBS. Afterwards, the antigen specific antibodies IgG and IgA were detected in sera and nasal washes, respectively. Subsequently, cell mediated immune responses were measured by the expression of CD69 activation marker on T-cells from immunized mice by flow cytometry. In general, the results demonstrated that chitosan nanoparticles could have potential in the mucosal vaccine development.

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The Multistep Process of Coating PCL Membranes with MXene Solution

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Electrospinning is a direct route to generate polymer-based fibers with diameters on the nano- to micron-scale. This method is very widely explored in biomedicine for applications, including drug delivery systems, tissue engineering, and regenerative medicine [1]. Polycaprolactone (PCL) electrospun biopolymer in biomedical applications has attracted considerable interest due to its biodegradability and biocompatibility [2]. The surface of such nanofibers can be further modified with molecular species or nanoparticles during or after an electrospinning process [3]. To provide polymer materials with conductivity for some special applications, MXenes (a new large family of 2D nanomaterials) should be used for electrospun material modification [4, 5].

Our investigation aims to determine the effect of MXene deposition on the morphology and biological properties of the electrospun PCL membrane. To improve the hydrophilic properties of the PCL membranes, they were treated with 20\% H\textsubscript{2}SO\textsubscript{4}. Then scaffolds were impregnated with a solution with Mxenes from one to three times. The properties of the treated membranes were evaluated with a Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS). The cytocompatibility of the samples was determined using an osteosarcoma cell line (U\textsubscript{2}OS).

After the treatment, SEM demonstrated an increase in nanofibers thickness and decreases porosity depending on repeated soaking. The EDS analysis detected a significantly high percentage of elements on the treated samples depending on the number of procedure repetitions. The presence of Ti\textsubscript{3}C\textsubscript{2} slightly affects promoting cell and biomaterial interactions. The cells cultured on the samples demonstrated high biocompatibility and the ability to support cell proliferation within five days of the experiment. Fluorescence microscopy provided visual evidence of cell proliferation levels depending on coatings number.

Functionalization strategy with H\textsubscript{2}SO\textsubscript{4} pretreatment allows a by-layer assembly of MXenes on electrospun nanofibrous scaffolds maintaining cell viability and metabolic activity on the treated samples. It is also essential to accomplish further studies to estimate the stimulating effect in applications for neural regeneration.

ACKNOWLEDGMENTS

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REFERENCES

Optimization Steps of Mucosal Vaccine Preparation using Polymeric Nanoparticles

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Abstract ID #NRA-0319

In recent years, there has been growing interest in the use of nanomaterials as drug carriers, mainly because of the benefits attributed to these materials. Polymer nanoparticle systems are capable of local and sustained administration for drug delivery, facilitate the improvement of the therapeutic index of drugs, and are capable of controlling drug release1. Proteins containing chitosan nanoparticles have potential in the field of targeted drug transport to the mucosa2. One of the parameters studied in the development of immobilized drug nanoparticles is the in vitro evaluation of drug release from a polymeric carrier, which is typically achieved by controlling the rate of polymer biodegradation (erosion) and drug diffusion from the polymer matrix3. Therefore, we aimed to find a suitable system with a high protein load and slow protein release. Here we show the preparation of nanoparticles from chitosan-TPP formed by ionotropic gelation and modified with PCL or hyaluronic acid and proteins (ovalbumin, epidermal growth factor). We characterized the prepared chitosan-based nanoparticles by measuring the DLS and the zeta potential. We then tested different methods of protein binding (encapsulation, adsorption, or chemical binding with carbodiimide) to chitosan-based nanoparticles. The mean nanoparticle size for chitosan and chitosan-PCL was 221.0 ± 46.61 nm (PI 0.52) and 231.9 ± 20.3 (PI 0.64) with a positive zeta potential of 41.69 mV and 36.72 mV. The binding efficiency using the BCA protein quantification assay was 45.39%, 44.2%, and 23.9% for chitosan-TPP protein encapsulation, chitosan-TPP protein sorption, and chitosan-PCL, respectively. Less than 10% of the protein was released from the particles in different pH buffers in the first 15 minutes, and then the release rapidly slowed. The results showed that chitosan-based nanoparticles with proteins could be suitable as a drug delivery system.

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Immune Compatibility of 2D Bismuthene Nanosheets for Future Combined Magnetic Hyperthermia and Photothermal Therapy

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Abstract #NRA-0330

Introduction: 2D pnictogens, including bismuthene, have recently emerged as new members of the ever-increasing 2D family thanks to their exceptional electronic, topological, thermoelectronic, and optical properties. Here we present a 2D bismuthene synthetized from the 3D bulk bismuth involving a surfactant-assisted chemical reduction method to specific improve its magnetic properties. Envisaging the future biomedical applications and considering the central importance of this material as a possible theranostic agent for photothermal and photodynamic therapy of cancer, the bio- and immune-compatibility of 2D bismuthene remains a fundamental step of its clinical translation. Methods: Here we applied our experience gained on 2D nanomaterials in this context [1–3] to evaluate the impact of 2D bismuthene on whole blood and immune cells by means of flow cytometry, complete blood counts and multiplex cytokine analysis.

Results: 2D bismuthene immune profiling on whole blood and functional studies with human peripheral blood mononuclear cells showed the excellent bio and immune compatibility of the material, as well as the ability to modulate the immune response with anti-inflammatory properties. Interestingly, the bismuthene did not boost the expression of activation markers on T cells and monocytes, but it actually reduced them. A significant decrease in the expression levels of CD69 and CD25 was observed for T cells and monocytes, giving proof a powerful CD25 expression of activation markers on T cells and monocytes.

Conclusions: Taken together these results describe bismuthene as a highly biocompatible 2D nanomaterial able to modulate the immune response with anti-inflammatory properties, a crucial aspect for the development of anti-inflammatory drugs and cancer nanotherapeutics [4–5]. As the link between cancer and inflammation is investigated, nanoscientists can engineer targeted nanomaterials to efficiently combat with the tumor-associated inflammation and cancer carcinogenesis, dissemination, and metastasis.

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MXene-mediated Immune Cell-Cell Interactions Revealed by Enzymatic LIPSTIC Labelling

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Abstract ID #NRA-0337

Among two-dimensional nanomaterials, the transition metal carbides/carbonitrides (MXenes) [1] have gained remarkable attention for their potential as biomedical nanotools [2, 3]. Due to their unique combination of physicochemical properties, MXenes enable a wide range of biomedical applications. Among these, we have recently explored the use of MXenes to fight against SARS-CoV-2 and have demonstrated the immune-modulatory properties of Ti3C2 MXene [4]. The comprehension of the biomolecular effects of MXenes on immune cells is a prerequisite for their exploitation in future translational applications. To characterize the complex interactions between MXenes and immune cells, we applied the Labelling Immune Partnerships by SorTagging Intercellular Contacts (LIPSTIC) [5] approach to nanomaterials (LIPSTIC). A key phenomenon in the immune response, the intercellular communication between T cells and antigen-presenting dendritic cells (DCs), was investigated after exposure to two highly stable and well-characterized MXenes: V2C3 and Ti3C2. Cell-specific intercellular communication between DCs and T cells was drastically decreased by the former which induced immunosuppression. Moreover, an anti-inflammatory activity of V2C3 was revealed by functional analyses and cytokine quantification. Our results open the way for i) new investigations on the promising immunomodulatory properties of novel MXenes in the context of autoimmune diseases and ii) a new methodological approach in nanotoxicology and nanomedicine.

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REFERENCES

Development of ZnO and ZnO-Au Nanoplatform for Detection of Listeria Monocytogenes and Klebsiella Pneumonia

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Abstract ID #NRA- 0339

Fast and quantitative detection of human pathogens in different environmental (soil, water, food) and biological (blood, urine) samples is still challenging, especially during the pandemic. Standard methods, such as microbiological, ELISA and PCR, are precise but expensive and require a long time [1]. This stimulates the development of new detection platforms. Optical biosensor planforms are a new generation of sensing devices due to their high precision and label-free concept. The optical biosensor platform requires specific material with advanced structure and optical properties for the effective signal transformation of biological interaction into a physical signal. Optical biosensors use absorbance and photoluminescence as measurement techniques. Combining nanomaterials with optical methods benefits from sensor platforms with high surface area and advanced optical properties. ZnO and ZnO-Au composites have attracted attention among different nanostructures due to their high isoelectric point and intense room-temperature photoluminescence [2]. Modifying the ZnO surface with Au nanostructures leads to new effects based on ZnO photoluminescence and SPR effects from Au nanostructures. Adsorption of biomolecules on the ZnO-Au surface is more sensitive than bare ZnO, which makes these nanostructures attractive for biosensor applications.

The aim of the current research was to develop nanostructured platforms (ZnO and ZnO-Au) for the detection of Listeria monocytogenes and Klebsiella pneumonia pathogens. ZnO nanorods have been deposited on glass surfaces by the drop-casting method. Gold nanolayer was formed on the ZnO surface by the UV reduction method of HAuCl4. Silanization of ZnO and thiolization of ZnO-Au were provided to make surface functional groups for binding specific antibodies. Structural properties of ZnO and ZnO-Au nanostructures have been studied by FTIR, SEM, and Transmission Electron Microscopy (TEM). Optical characterization of ZnO and ZnO-Au was performed by using UV-vis diffuse reflectance and photoluminescence (PL). Interaction of the sensor surface with Listeria monocytogenes and Klebsiella pneumonia pathogens was studied by photoluminescence spectroscopy. The sensitivity and selectivity of the sensor were analyzed. Both ZnO and ZnO-Au nanoplatforms demonstrate appropriate optical parameters and could be used to develop highly sensitive optical nanosensors for the Listeria monocytogenes and Klebsiella pneumonia.

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REFERENCES

Nanostructure Polypyrrole Formation: Dye-assisted Synthesis with Methylene Orange as Effective Structure Guiding Agent

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Abstract ID #NRA-0340

Polypyrrole (pPy) being carbon-based nitrogen containing polymeric material is known for its protective [1] and sorptive [2] properties. Being stimuli-responsive material it is willingly used as biosensing platform [3], drug delivery matrices [4], artificial muscles component [5]. The properties of the pPy are strongly dictated by the morphology of material which can be tailored by the choice of the synthesis condition in terms of additives, oxidative agent or type of doping ions. Many studies were done to find the additives capable to induce structure organization within the polymer chains with organic dyes being most promising ones. Among them methylene orange (OM) was found to be the most interesting owing its structure guiding ability as it is named as soft sacrificial template. However, there is lack of detailed studies related to the influence of concentration of MO on the assemblies ability of pPy chains as well as time of the synthesis.

Here we show results of the studies for series of pPy synthesized by a dye – assisted chemical route in a presence of MO with various concentration. The material was obtained in an aqueous solution in respect to green technology approach. We showed that the ability of this dye to induce organization in pPy is strongly concentration dependent (in terms of MO) with changing content of the globular and nanotube structures in a final product. The organization influences also the effective length of π-conjugation along the polymer chains. It was calculated based on the ratio of intensity of FTIR peaks corresponding to antisymmetric and symmetric stretching vibrations in the pyrrole ring (1578 cm⁻¹ vs 1479 cm⁻¹). The results revealed that at low template concentration the conjugation length was lowered while only after reaching the highest concentration the desired enhancement in conjugation length was induced. The observation was supported with XRD analysis that revealed peaks of the semi-crystalline phase in the samples deposited in the presence of high-concentration of MO template. Our results demonstrate the profound impact of the concentration of the MO soft template on the morphology of the polypyrrole. It shows the possibility to induce nonorganization within molecular structure of the conducting polymer that influence markedly on macroscopic properties like conductivity. We anticipate that our study is a reference point for a vast majority of polypyrrole users that allows to point the mutual dependency of the synthesis condition and morphology of the material.

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REFERENCES

Surface Modification of Luminescent Porous Silicon by Aqueous Solutions of Amino Acids

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Abstract ID #NRA-0341

Siliceous nanomaterials, including porous silicon (PS), are promising for modern biomedical applications, such as drug delivery, bioimaging, tissue engineering, and biosensors [1, 2]. They have attracted a lot of attention due to simplicity of their synthesis, unique physicochemical properties and good biocompatibility. Amino acids were proposed to functionalize the surface of siliceous porous nanoparticles, for example, to modify their surface charges [3]. However, amino acid effect on degradation and oxidation of PS in water ambient were not studied to date. In our work, interaction of PS with aqueous solutions of some amino acids with non-polar radicals (glycine, alanine, valine), including aromatic one (phenylalanine), was studied by means of absorption and photoluminescence (PL) spectroscopy, which monitored modifications of the PS surface composition and changes in the nanostructure size, respectively. An increase in PS PL and shift of the spectrum peak towards higher energies were found after the treatment by all the used amino acid solutions. The most prominent changes in PL were revealed for glycine. Although much weaker, but similar changes in PL were observed after a treatment of PS with deionized water. It was also shown that the presence of amino acids, unlike distilled water, leads to changes in the PS PL accompanied by significant oxidation of the PS surface. The behavior of PL is well explained within the quantum-size model in terms of decrease in the size of the emitting silicon nanocrystallites as a result of the interaction with the aqueous solutions. Degradation and oxidation of the PS are assumed to be the immediate cause of the decrease in the nanocrystallite sizes. The results allow to conclude that amino acids are involved to both the processes. Firstly, presence of amino groups in the amino acids enhances the PS degradation. They are nucleophiles and may attack PS. Such an effect manifests for all the studied amino acids to the same extent. Secondly, amino acids, especially glycine, may stimulate formation of reactive oxygen species in aqueous solutions, thus leading to PS oxidation. So, the obtained data allow to estimate an effect of the studied amino acids on the PS interaction with water environment and take it into account when using PS as a drug carrier and applying it to accelerate PS biodegradation.

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Biomedical Applications of Two-Dimensional Materials: MXene Immunocompatibility

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Abstract ID #NRA- 0345

Two-dimensional (2D) transition metal carbides/carbonitrides (MXenes) are rapidly growing as promising nanotools in biomedicine. [1-4] Considering the central importance of the immune response for the clinical translation of nanomaterials, we evaluated the effects of three different MXenes (Mo2Ti2C3, Nb4C3, and Ta4C3) ex vivo on human peripheral blood mononuclear cells (PBMCs).

We assessed the immunocompatibility and the immune cell functionality by measuring 40 cytokines by Luminex technology. The materials exhibited only a slight modulation on the inflammatory mediators analyzed. Next, we investigated their effects on PBMC by mRNA sequencing. By performing principal component analysis on all analyzed transcripts (N=19,959), we found that MXene-treated samples clustered close to the controls, and separately from concanavalin A (ConA)- and lipopolysaccharide(LPS)-treated samples, thus indicating that only minimal perturbations were induced by the materials. Overall, we did not observe genome-wide changes induced by MXenes. All materials showed modest effects on PBMCs, modulating the expression of fewer genes than the positive controls ConA and LPS. In particular, even if all materials had similar effects on gene expression modulation, Ta4C3 had slightly greater effects than Mo2Ti2C3 and Nb4C3. The expression of 142, 46, and 83 genes was modulated by Ta4C3, Mo2Ti2C3 and Nb4C3, respectively, whereas the positive controls ConA and LPS modulated the expression of 4,340 and 710 genes, respectively. Furthermore, pathway-enrichment analyses on genes coherently modulated by the materials showed only modest enrichment of immune-related pathways without a clear indication of activation or inhibition.

Our results provide a compendium of knowledge on the biocompatibility of MXenes for the safe development of nanosystems in biomedicine.

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Research Ethics and Nanomedicine: Framing Responsible Conduct of Nano-Studies

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Nanomedicine provides extraordinary opportunities for advanced diagnostics and effective therapy. However, rapidly evolving nanomedical technologies and products generate ethical and regulatory concerns due to unique risks and uncertainties not faced in other fields of biomedical research [1]. This study aims to discover ethical aspects of clinical research in nanomedicine through the ethical principles for clinical research articulated by Emmanuel EJ [2].

The scientific validity of the study is an essential ethical requirement, especially in human research. Breakthroughs in nanotechnologies have accelerated the pace of nanomedical studies and translation to clinical settings. However, aside from the standard requirements for justifiable research, nanomedical trials need additional considerations on the hazards, risks assessment, and safety [1, 3]. Even before the clinical trials, the researchers working with nanomaterials are exposed to them and meet the potential danger of unexplored biological or toxic effects of nanoproducts. So detailed risks-benefits assessment and disclosure, actions for minimizing risks and additional protection of research subjects are essential for nanomedical studies. These aspects, along with study design and population, should be evaluated carefully during an independent review of the study protocol. The multidisciplinary nature of nano-studies also raises the question concerning the specific requirements for an independent review board, especially considering the unexpected risks and uncertainties of nanomedical studies [3].

A proper communicative partnership between researchers, industry, community, and health policymakers is essential for nanomedical studies. This principle addresses both the responsibility for implementation and affordability of nanomedicines, usually expensive and unevaluable for the poor. There is a need in promoting justice in terms of fair access to nanomedicine [3]. These nuances also address the principle of social value. Although nanomedical technologies have revolutionized diagnostics and brought effective treatment options for many groups of people, it also poses some risks, as invisible and pervasive nanomaterials can affect the environment in a long-term manner. Finally, translating nanomedical solutions to clinical practice should follow the ethical imperatives of fair participant selection, an appropriate informed consent process with complete disclosure of possible and unexpected risks and corresponding protective measures for participants and communities.

To sum up, clinical studies in nanomedicine relate to substantial ethical issues comprising risk assessment and fair distribution of nano-studies benefits. Besides, communication between academia, industry and society is essential for minimizing risks to the environment and protecting researchers, participants and the community from the possible adverse effects.

REFERENCES

Preparation and Characterization of New Nanocomposites Applicable in Bone Tissue Regeneration

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Abstract ID #NRA- 0350

For a long time, dental surgery has been using methods of restoring missing teeth with the use of implants. The enormous development of material engineering and nanotechnology enables the development of durable and safe materials, which at the same time provide great functional and aesthetic effects [1]. However, the success of implantological treatment depends on many factors, including the skill of the surgeon, the degree of complexity of the treated defect, the biomaterial used, and the patient’s health, including, in particular, the condition of the bone tissue in the jaw. It is a particularly tremendous problem in patients suffering from osteoporosis or bone loss caused by the loss of teeth in the period from several years before the start of implant treatment. In this case, before treatment, it is necessary to rebuild the bone tissue in order to create structures that enable the mechanical positioning of the implant screw. Such process is called a bone augmentation [2].

Bone augmentation is a procedure performed, as a rule, before the initiation of implant treatment, especially when the patient’s bone tissue is insufficient for the correct implantation of the implant. This situation occurs in particular in patients suffering from advanced periodontal diseases leading to damage and loss of bone tissue, as well as after tooth extraction, when bone atrophy occurs during alveolar healing and with advanced periapical lesions.

The use of 3D printing makes it possible to obtain materials with strictly programmed properties tailored to the individual needs of the patient, and therefore it is an increasingly personalized medicine [3]. In addition, it enables the preparation of nanocomposites enriched with nanoparticles that stimulate the growth of bone tissue and prevent inflammation or bacterial infections, as well as improve mechanical properties.

The main aim of this research was to develop new nanocomposites based on biocompatible and biodegradable thermoplastic polymers doped with chitosan derivatives and nanoparticles of hydroxyapatite and titanium dioxide. The obtained nanomaterials were characterized in terms of their chemical structure, spatial structure and biological properties. The prepared materials had an appropriate three-dimensional structure enabling the adhesion and proliferation of cells, enabling the reconstruction of bone tissue.

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Phase Composition and Magnetic Properties of FeOOH/$\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$/γ-Fe$_2$O$_3$ Based Nanoparticles in a SiO$_2$ Shell for Biomedical Application

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Abstract ID #NRA-0354

Applications of nanotechnology in the design of new biomedical devices span several interdisciplinary areas of nanomedicine, diagnostics, and nanotheranostics [1]. In this work, we investigate the structure and magnetic properties of core-shell nanoparticles (NPs), containing Gd doped iron oxides cores, covered with SiO$_2$ shells. Nanopowders of pristine and silica-coated Gd$_x$Fe$_{2-x}$O$_3$ oxides with $x = 0, 0.033,$ and 0.066 were fabricated by the coprecipitation method. Silica shells were created by tetraethyl orthosilicate (TEOS) hydrolysis [2]. The synthesized samples were annealed at the temperature $T = 240 \, ^\circ$C for 4 hours in the 1.7 Pa vacuum [3]. They were characterized with a scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction analysis (XRD), 57Fe Mössbauer spectroscopy (at room temperature (RT) and at 20 K), and with vibrating sample magnetometry (VSM) in the range of temperatures 2-300 K and magnetic fields up to 9 T. SEM and EDX images indicate the formation of microsized agglomerations of nanoparticles with a uniform distribution of gadolinium. The obtained XRD patterns of the samples before annealing indicate the presence of two phases: FeOOH and $\gamma$-Fe$_2$O$_3$. Annealing of the nanoparticles resulted in the transformation of FeOOH phase to $\alpha$-Fe$_2$O$_3$. The best fit of RT Mössbauer spectra of initial Gd$_x$Fe$_{2-x}$O$_3$ nanopowder is obtained in the assumption of four subspectra: central nonmagnetic doublet, one unsplit, and two split sextets (Heff 1 = 49.2 T, Heff 2 = 45.5 T). Gd doping results in the formation of two distinct sextets characterized by Heff 3 = 35 T and Heff 4 = 30 T. RT Mössbauer spectra of silica-covered nanoparticles of all compositions are generally quite similar to those recorded for Gd$_x$Fe$_{2-x}$O$_3$ samples. Obviously, hyperfine parameters extracted from the spectra are very close both to those of Fe oxide and FeOOH phases. However, the assignment of subspectra to specific phase is complicated due to possible superparamagnetic effects. Mössbauer spectra at $T = 20 \, ^\circ$K for all samples studied could be fitted with two well-resolved magnetic sextets with Heff 1 = 49.2 T and Heff 2 = 50 T which could be assigned either to Fe-oxide and or to FeOOH phase. At the same time, Mössbauer spectra of silica-coated nanoparticles after annealing clearly reveal the conserved contribution of the doublet and magnetically-collapsed subspectrum. Magnetic properties of the annealed NPs were characterized by the DC mass magnetic susceptibility ($\chi$) measurements in the temperature range from 2 K up to 300 K and DC mass magnetization (M) measurements as a function of a magnetic field at selected temperatures. Doping with gadolinium leads to a linear increase of magnetization at 9 T and 2 K (2.4 → 2.9 → 3.2 $\mu$ B/f.u., respectively) but it doesn't change its values at RT which differs from the results given, for example, in [4].

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Electrospun Scaffolds with Hydroxyapatite for Guiding Bone Regeneration

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Abstract ID #NRA- 0355

In this presentation I will give an overview of biomaterial strategies to produce 3D scaffolds for bone research to better understand and manipulate their structural and mechanical environments. Natural bone has a complex nanostructure with a twisted plywood arrangement of collagen and hydroxyapatite, which provides bone’s toughness and resistance to fracture. This structure is difficult to re-create in the laboratory which means that tissue engineered bone is usually dis-organised and weak. Here I will describe scaffolds fabricated by electrospinning from polycaprolactone or polyurethane in aligned or non-aligned formats. Composite scaffolds include hydroxyapatite micro and nanoparticles which further support bone deposition [1]. We find that alignment can be used to guide bone-like collagen orientation in these in vitro systems. Interesting differences can be observed between cell responses at different stages of cell differentiation [2]. Using second harmonic generation imaging we observed a unique twisted plywood arrangement of collagen fibres in our in vitro system. Furthermore, we used these scaffolds to understand diseases of collagen mal-formation such as osteogenesis imperfecta (brittle bone disease) [3]. We found that cells from osteogenesis imperfect patients are not able to align as well on electrospun scaffolds, this provides a 3D format in which therapeutic options for this disease can be studied.

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Nanomedicine Strategies to Target Anticancer and Antimicrobial Therapies

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Abstract ID #NRA-0384

The problem of increasing drug resistance arises not only in the treatment of bacterial infections, but also often concerns fungal, viral or cancerous diseases. There is an urgent need to develop new medical strategies using properly designed chemotherapeutic agents and functional materials allowing for effective therapies in the era of increasing drug resistance. No less important is the targeted and controlled delivery of chemotherapeutic agents as well as the initiation of the desired mechanisms of their activity. Such possibilities are provided by the wide tools of nanomedicine.

The topic of the presentation will focus metals in advanced nanomedicine strategies for the needs of anticancer and antimicrobial therapies. Three main research topics will be presented: 1) nanoformulations of Cu(I), Cu(II), Ru(II), Ir(III) complexes with phosphine-based ligands for anticancer treatment [1, 2], 2) hybrid biocompatible materials based on metal nanoparticles (i.e., Ag, Au, Cu) and biopolymers (e.g., chitosan) for infections treatment [3], and 3) polymeric nanoformulations for controlled delivery of bioactive molecules for medical applications [4, 5]. The synthesis and physicochemical (important from the point of view of medical applications) as well as biological in vitro characteristics of new nanosystems will be presented and discussed in details.

The proposed and experimentally proven mechanism of biological activity of the obtained nanoformulations of metal complexes based on multiple pathways and simultaneous action on many cellular targets (e.g. production of reactive oxygen species, DNA fragmentation, activation of the mitochondrial apoptotic pathway) renders these nanosystems among interesting and promising in the fight against drug resistance. On the other hand, the tested biocompatible nanocomposites based on metal nanoparticles such as Cu, Ag and Au and chitosan are promising new functional materials combining bacteriostatic action of a polymer carrier with bactericidal metal nanoparticles. Examples of applications relate to the use of these materials as anticancer nanoformulations, dressings, or coatings to functionalize medical surfaces.

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Application of Hybrid Polymer-Oxide Coatings in Surface Modification of Titanium Implants for Animals

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Abstract ID #NRA-0418

Dental implantology is one of the most dynamic and rapidly growing specialties in medicine and veterinary medicine. With the development of implantology, there is an increasing demand for long-term implants for animals, i.e., implants that can stay in the animal’s body for the rest of its life. Animals, compared to humans, are quite demanding patients, due to their high vitality and activity that causes their bones to carry significant loads. Titanium-based materials are commonly used for bone tissue implants. This material is distinguished by its good corrosion resistance, which is very beneficial due to the chloride environment of the body fluids [1]. Titanium and its alloys are characterized by good mechanical strength, biocompatibility, osseointegration ability, and low elastic modulus (i.e., 48-112 GPa) compared to other metallic biomaterials [2].

To increase the bone tissue integration rates of the implant, the surface of titanium implant is modified. Anodic oxidation processes, such as plasma electrolytic oxidation (PEO) allows for the formation of a bioactive, porous oxide layer on the surface of the implant to facilitate the osseointegration process [3].

The implant surface should also have antibacterial or at least bacteriostatic properties to prevent infections to which the body is exposed during the implantation procedure. One method to obtain such properties is to apply a degrading polymer coating containing antibiotics on the porous oxide layer produced in PEO process on implant surface. In this research titanium dental implants were oxidized using the plasma electrochemical oxidation technique in a 0.1 M Ca(H₂PO₄)₂ solution at a voltage of 350 V and a current density of 100 mA/cm². The process was carried out for 5 min. Anodized Ti implant was immersed in poly(adipic anhydride) (PADA) solution with controlled immersion and withdrawn rate. The implants were immersed in a chloroform-polymer solution at different concentrations (0.5% or 1% by weight) with 5 wt.% amoxicillin. The amount of drug released from the polymer coating was analyzed by high-performance liquid chromatography. The concentration of released amoxicillin from the polymer matrix was 2.94 μg/mL, 3.20 μg/mL, 3.39 μg/mL after 1 h, 4 h and 6 h of exposure in PBS (phosphate-buffered saline) solution, respectively.

The amount of drug released from the coating (1 h immersion) inhibited the growth of reference Staphylococcus aureus ATCC 25923 and Staphylococcus epidermidis ATCC 12228 bacteria, and the zones of inhibition ranged from 17 mm - 23 mm. Analysis of S. aureus ATCC 25923 bacteria adhesion to the implant surface showed that much lower bacteria (4.6×10² CFU/mL) were adhered compared to non-modified implant (5.6×10⁵ CFU/mL).

The most favorable coating on the dental implant is formed when a solution of 1 wt.% PADA with 5 wt.% amoxicillin is used.

ACKNOWLEDGMENTS

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REFERENCES

Optimizing the Osteogenic Potential of TiO$_2$/Hydroxyapatite Coatings with Design of Experience

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A common way to improve osteointegration of spinal implants is to coat them with osteoinductive materials like TiO$_2$ or hydroxyapatite (HAP). Tuning the coating’s composition and process can help amplifying said osteoinductive effect. For example, introducing Mg$^{2+}$ and Sr$^{2+}$ ions into the HAP structure can, respectively, stimulate osteoblasts and inhibit osteoclasts [1]. Furthermore, the original coating conditions can alter the properties of sol-gel coatings, including their biologic performance [2]. This work aims to study how the osteogenic potential of composite sol-gel TiO$_2$/HAP coatings can be improved by independently studying the effect of HAP composition and of the coating conditions on the differentiation of hTERT-MSCs Y201 [3]. Each study will use a different Design of Experiences (DoE) approach, using Alkaline Phosphatase (ALP) activity of cells at day 14 as the response. It was shown that HAP synthesised with 10% Mg substitution, 5% Sr substitution and 15 ml of Ammonia solution 28% significantly increased ALP activity when compared to commercially available Mg-enriched HAP (Mg-HAP). Furthermore, it was shown that a TiO$_2$/HAP ratio of 1:1.5 (w/w) increased ALP activity of coated substrates, as well as a higher number of deposited layers, faster heating rates when sintering, and faster dipping cycles. Overall, it is theoretically expected that the combination of the best performing HAP and coating conditions will increase the differentiation potential of Y201 cells by 140% when compared to uncoated substrates, and by 72% when compared to coatings prepared with Mg-HAP.

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REFERENCES

Discovery of Memristive Biomaterials for Sensory Aims

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The true discovery of memristive biomaterials for sensory aims has been made kind of 10 years ago. This Lecture shows the temporal perspective of this totally new field of research, which abruptly emerged along the course of the last decade. More in detail, the Lecture starts with the introduction of the concept of “memristor” as a two-terminal fundamental component of electrical circuits, which presents a resistance that keeps a memory on past-applied voltages. The memristor has been initially envisaged and theoretically defined in early 70s already, while the concept remained almost un-addressed for the following 50 years. A series of new materials demonstrating the memristive effect have been discovered only starting from 2008 onward. In particular for sensory aims, the combination of memristive nanowires, made in silicon and nickel by nanolithography and selective chemical etching, with recognition biomolecules, such as antibodies and aptamers, provided the best ever demonstrated sensing of disease biomarkers and therapeutic compounds. The very first worldwide ever-reported electrochemical ultrasensitive detection of the cancer biomarker called Prostate-Specific Antigen (PSA) with an unprecedented Limit of Detection (LoD) down to 23 aM has been published in 2016 [1], and still is an unbeaten record in literature. One year later, the very same technique has been applied for the effective ultrasensitive detection of the Tenofovir, an antiviral compound often used to treat HIV and chronic hepatitis, obtaining a LoD of 3.4 nM only in undiluted human serum [2]. These detections were 10 times better performing with respect to any alternative sensing method ever published previously in literature for the electrochemical detection of these compounds. To explain the reasons of such amazing performances never seen before by using similar kind of biomaterials but instead combined with semiconducting or metallic non-memristive nanowires, a new theory about the physics of such memristive biomaterials [3] is then discussed in details in this Lecture. The appearance of the main sensing parameter, called “voltage gap”, is thus explained in terms of diffusion currents, both in the bulk of the nanowires and at the interface with the biomaterials. The voltage gap is then related to voltage-induced charge-injection in the materials, coherently with the memristive phenomena. Furthermore, an equivalent circuit for the electrical behaviour is introduced as well to demonstrate that these exceptional sensing capabilities are also due to effects related to diffusion capacitances. The Lecture closes proposing the very first pioneering co-design of memristive biomaterials and CMOS circuits, typically required to realize full-automated detections of multiple cancer markers (e.g., granzymes and interferon-γ; or PSA and PSMA, the variant of PSA found in cell membranes) for a better stratification of tumor patients [4] and a simultaneous computation of cancer risks [5].

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REFERENCES

Printable Magnesium and Strontium Substituted Hydroxyapatite-Polycaprolactone Composites

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Currently hydroxyapatite is used as therapeutic tool in orthopaedic medicine as a bone graft substitute or a coating to support tissue implant-attachment. Even though hydroxyapatite (HAP) is routinely used in vivo, its slow degradation rate compromises its osteogenic activities when used as bone filler [1]. In this project we aim to create a HAP that is substituted with magnesium and strontium (sHAP) to increase its solubility, osteogenic integrity and bioactivity. To create printable polymer composite, we incorporated sHAP into a polymer matrix based on polycaprolactone (PCL).

HAP was synthesized by a wet, continuous method in a mixing column using orthophosphoric acid and calcium hydroxide as phosphorous and calcium precursors, respectively, and magnesium nitrate and strontium nitrate as Mg and Sr precursors. The successful synthesis of sHAP was evaluated via Fourier-transform infrared spectroscopy (FTIR) and inductively coupled plasma optical emission spectrometry (ICP-OES). Crystallinity was analysed via X-ray diffraction (XRD). Different wt% of sHAP (10%, 30%, 50%) were incorporated into a 4-arm methacrylated PCL matrix to create a printable composite. Printability of the ink was modified by increasing its shear-thinning character via the addition of hydrophobic silica (1.5%). Scaffolds with the dimensions 7.5 mm x 7.5 mm x 0.69 mm were printed in a 3D mesh pattern, sometimes called a ‘woodpile’ via an extrusion printer and cured under UV light. In vitro experiments were performed using Y201 human mesenchymal stem cells (hMSCs) [2] under serum free conditions.

sHAP could be successfully fabricated with high amounts of Mg and Sr incorporated. However higher substitution lowered overall synthesis success with decreased amount of substituents entering the lattice structure and the synthesis of other calcium phosphates rather than HAP. The fabrication of 3D 2-layer sHAP-PCL mesh scaffolds could be achieved via 3D printing, showing good printability and definition with a line width of 400μm and 250μm distance between lines when using hydrophobic silica as shear-thinning agent. sHAP-PCL scaffolds showed no cytotoxicity in vitro on Y201 MSC.

sHAP-PCL 3D printed scaffolds have no cytotoxic effects and have the potential to support osteogenesis of hMSCs for bone repair. These composite inks have the potential to be tuned for the synthesis of scaffolds for various applications such as bone graft substitute to fill spinal cages for improved spinal fusion.

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The "Synthetic Coral": Opportunities for Nanomaterials in Coral Biology

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In the “synthetic coral” project [1], bioengineering of natural systems are studied because of their potential to reveal new strategies to combating anthropogenic impacts, such as the decline in coral reefs. This requires an interdisciplinary approach including the development of new immersive collaborative environments [2]. This presentation will address emerging opportunities for nanomaterials research by harnessing the big data revolution and apply convergent methods from data-driven manufacturing to build a "synthetic coral" [1] as an integrated computational and experimental validation system. Focusing on the stony coral Pocillopora damicornis, results from remote homology detection to relate coral holobiont proteins to functions such as detection of light of different wavelengths will be presented [3]. Motions of coral motion have been quantified using techniques derived from aerospace engineering [4,5] and was used to validate predictions of visual function [3]. Growth of coral cells on different engineered substrates has been standardized [6] opening the door to pharmacological studies of corals [7]. Insulin and nanoparticle toxicity have been studied using optimized conditions [8]. This integrated prediction-validation cycle will help to unravel the nature of how corals grow and respond to stress and provide a novel platform for materials discovery.

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Conference Track: “Nanobiomedical Research & Applications”
Anisotropic Magnetic Particles for Nanomedicine Applications

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Abstract ID #NRA-0451
Magnetic nanoparticles have been building blocks in applications ranging from high density recording to spintronics and nanomedicine. Magnetic anisotropies in nanoparticles arising from surfaces, shapes and interfaces in hybrid structures are important in determining the functional response in various applications [1]. In this talk, I will first introduce the basic aspects of effective anisotropy and measurements through RF transverse susceptibility experiments. Tuning magnetic anisotropy has a direct impact on the performance of functional magnetic nanoparticles in biomedical applications such as enhanced MRI contrast and magnetic hyperthermia cancer therapy. There is a need to improve the surface functionalization and specific absorption rate (SAR) or heating efficiency of nanoparticles for cancer diagnostics and therapy. Strategies going beyond simple spherical structures, such as exchange coupled core-shell nanoparticles, nanowire, nanotube geometries can be exploited to increase saturation magnetization, effective anisotropy and heating efficiency in magnetic hyperthermia. This talk will combine insights into fundamental physics of magnetic nanostructures along with our recent research advances in their application in cancer therapy and diagnostics in nanomedicine.

REFERENCES
Biocatalytic Properties of “Enzyme-Nano Complexes” Based on ZnO/Ag and ZnO/Fe Nanoparticles with Immobilized Peroxidase

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Currently, there is a growing interest in nanomaterials modified with enzymes and other active substances [1]. Enzyme-nano complexes allow to combine the functions of biomaterial and unique properties of nanomaterial [2]. Multiple uses of the enzyme reduce the final cost of biocatalysis [3], immobilization strengthens the structure of the system and the system can be easily recovered from the reaction mixture [4]. These goals can be achieved by enzyme-nano complexes, which makes them interesting topic of research. They are used as antibacterial and photocatalytic additives in coatings and many other industries [5]. These materials are also widely used in photocatalytic removal of pollutants from aqueous environments, among which pharmaceuticals are particularly challenging [6].

One of the most commonly used nanomaterials is zinc oxide nanoparticles (nZnO). It is chemically and thermally stable and has good mechanical properties [7] Zinc oxide nanoparticles are able to effectively absorb light in the UV range and can be used to improve the absorption efficiency of visible light, so they have good photocatalytic properties [8]. Among the various metals, silver has gained the most attention because its doping enables the activation of the photocatalyst in visible light, and also it imparts antimicrobial properties to the entire material [9]. As another modifier, iron can be used, which in addition to improving the photocatalytic properties is present in horseradish peroxidase (HR-POX) contains a prosthetic group in the ionic form The enzyme can catalyze the oxidation of a wide range of substances with the help of H2O2. Zinc oxide nanoparticles due to their high specific surface area, chemical stability, and inertness are a good candidate as a base for HR-POX immobilization.

This research presents the preparation of a photocatalyst based on ZnO nanoparticles modified with silver and iron ions and peroxidase. The materials were characterized using XRD, AAS, TEM, FTIR, and UV-Vis analyses. Metal ion sorption analysis revealed that Ag and Fe ions were successfully adsorbed on the ZnO surface, reaching sorption capacities of 13.39 mg/g and 41.47 mg/g, respectively. After immobilization of peroxidase on the materials, final ZnO/Ag/POX NPs and ZnO/Fe/POX NPs were obtained, presenting peroxidase activities of 291.34 and 223.78 U/g, respectively. Based on the ibuprofen decomposition study, the effectiveness of the photocatalysts was confirmed. After 120 min, the decomposition efficiency of ibuprofen with an initial concentration of 20 mg/L in the presence of H2O2 additive was 78 and 86% for ZnO/Ag/POX NPs and ZnO/Fe/POX NPs, respectively. The highest activity was exhibited by ZnO/Fe/POX NPs, whose activity increased by 40% after the addition of H2O2 additive. It is suggested that the high activity of the material is due to two separate processes taking place: the Fenton reaction and the decomposition of H2O2 by peroxidase.

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Nanohybrids of Metal Oxides-Polysaccharide and their Biostatic Properties

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In view of the growing global problem with the spread and increase in the number of strains of microorganisms acquiring resistance to antimicrobial substances, it is particularly important to search for substances with antimicrobial activity to which pathogens cannot develop resistance. Such substances may, in the future, be used as an important component of modern antimicrobial preparations or materials such as for example coatings or construction materials, reducing the acquisition of drug resistance and limiting spread of pathogenic microorganisms [1, 2].

Hybrid nanomaterials are synthesized by the combination of two or more components, such as for example inorganic and organic nanoparticles combinations. The properties of the obtained nanohybrid can be shaped by selecting the components of the hybrid according to their properties. Interactions between the selected ingredients can lead to unique properties not present in any of the original components. As a result, undesirable features can be eliminated and it is possible to obtain expected properties that are new to relative to the base materials [3–6].

The aim of this study was to synthesize inorganic-organic nanohybrids and obtain materials with antimicrobial effects. Nanoparticles of chitosan (CS) was deposited on nanocomposite carriers such as calcium oxide with titanium dioxide (CaO–TiO₂) and copper(II) oxide with titanium dioxide (CuO–TiO₂). The efficiency of the process was examined at varying concentrations of chitosan and temperature and analysed statistically. For further stage of research, the parameters for nanohybrids synthesis were selected based on the highest amount of nano-chitosan deposited on the nanohybrids – for each carrier, the process conditions were as follows: chitosan solution at 5 g/L and 20 °C. The materials were obtained using these parameters and were used for microbiological tests against E. coli ATCC 25922, S. aureus ATCC 25923 and C. albicans ATCC 10231. The growth inhibitory activity of the obtained materials was qualitatively defined. These results suggest that the synthesized nanohybrids and nanocomposites exhibit biostatic action. Especially outstanding of the tested materials are CuO–TiO₂ and CuO–TiO₂–CS, demonstrating a broad and strong inhibitory effect on microbial growth at low applied concentrations (1250 μg/mL). Moreover, the CaO–TiO₂–CS nanohybrid is characterised by a significantly improved performance compared to the unmodified CaO–TiO₂ composite [7].

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TRACK 12
“THEORY & MODELING”
MoS$_2$ Oxidation Effect: Theoretical and Experimental Studies

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Two-dimensional (2D) materials have drawn significant interest due to their unique structural, electronic, and optical properties. Changes in their structure occur during intentional modifications as well as under the influence of exposure to the environment, such as oxygen in the air. We study the effect of the implementation of the oxygen atoms in molybdenum disulfide (MoS$_2$) flakes structure theoretically using density-functional theory (DFT) methods and the outcomes were confronted with the results of experimental research.

MoS$_2$ nanoflakes with stoichiometry $\text{MoS}_{2n}$ were optimized using the DFT method and the process of gradual substitution of oxygen in place of sulfur atoms has been simulated. We reported quantum-chemistry calculations of the modified MoS$_2$ monolayer which indicates that oxygen forms bonds with molybdenum until the formation of stable molybdenum oxide (VI) MoO$_3$. Experimental results confirmed the implementation of a new chemical compound in the MoS$_2$ 2D structure. The experiment was recreated by implanting a MoS$_2$ sample CVD grown on sapphire with O$^{2+}$ ions using the Secondary Ion Mass Spectrometry (SIMS) technique. SIMS measurements with sub-nanometer resolution confirmed the existence of five MoS$_2$ and the drastic damage in their outer layers after oxygen implantation. Annealing of the sample resulted in an almost complete reconstruction of the structure. Using the Raman spectroscopy technique we have demonstrated that residual oxygen was stabilized with the formation of the new chemical bonds in the structure of the 2D material.

It is found that 2D materials could be successfully investigated using a combination of experimental and theoretical techniques. We showed that by selecting the appropriate oxygen implementation parameters, it is possible to selectively oxidize MoS$_2$ and form MoO$_3$ at a selected depth, and thus create a semiconductor / insulator heterostructure. Quantum chemical techniques made it possible to predict the oxidation effect of MoS$_2$ towards MoO$_3$, while the use of instrumental techniques determined the area of occurrence of the most significant changes in the structure.

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Computational Studies of Cellulose Molecules Adsorption on the Surface of Carbon Nanostructures

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Abstract ID #TM-0108

Nanocomposite materials based on cellulose and carbon nanostructures (CNs) are currently actively studied as perspective multi-functional materials [1]. However, despite intensive studies, several critical problems regarding the peculiarities of the interaction of the components of nanocomposites “cellulose-CN” remain unsolved. These are, in particular, the questions regarding the types of bonds formed in the material between the components and the mutual influence of the components on their physical (electronic, optical, and other) properties. The aim of this work is to clarify such questions using computational research methods.

The contribution presents the results of theoretical studies of the interaction of cellulose molecular clusters with carbon nanomaterials: carbon nanotubes and graphene. The studies are carried out in the form of calculations of the electronic structure performed by the quantum chemical method in the DFT approximation [2]. The analyses revealed the mechanisms of adsorption of molecular cellulose on the surface of carbon nanotubes CNT(5,5) and single-layered graphene sheets, both bare and doped with boron or nitrogen. Binding energies and inter-nuclear distances between adsorption components are calculated and analyzed. The types of interatomic bonds between adsorbed cellulose molecules and carbon surfaces are elucidated.

It was found that the adsorption of cellulose molecules on the surface of undoped CNTs should generally be considered unlikely, as calculations show the absence of covalent interatomic bonds. Interaction of cellulose molecules with graphene surface should be more pronounced if compared to the case of nanotube surface because the obtained interatomic distances between cellulose and graphene atoms are significantly shorter. In general, the interaction of cellulose components with the surfaces of carbon components of composite materials should be considered relatively weak. However, this interaction can be somewhat enhanced by additional carbon surfaces doping by non-isovalent substitution impurities, boron, e.g., Obtained data are discussed in comparison with experimental data obtained from reflection and photoluminescence measurements performed under “nanocellulose”-graphene” nanocomposites films. Discussion regarding the possible influence of doping and surface functionalization of carbon nanostructures on cellulose adsorption characteristics is presented.

REFERENCES

Tricritical Behavior of BaTiO$_3$ upon Phase Transition

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Perovskite ferroelectrics are widely demanded in photonics, nonlinear optics, solar cells, nonvolatile memory, and laser equipment [1]. The state of the domain structure significantly affects the physical properties of ferroelectric necessary for modern device making. Classical methods for controlling the domain ordering are based on imposing intense external fields on a thermodynamically stable single-domain sample. But the growth of domains outside the electrodes and the retrieval of the structure to the original state [2] force us to look for new approaches to control the domain ordering.

Here we show that the influence of a weak hydrostatic pressure on the nonequilibrium barium titanate crystal quenched below Curie temperature (403 K) can be used to obtain domain structures with given parameters. Within the framework of phenomenological theory using differential scanning calorimetry, we established that phase transition in barium titanate has a tricritical behavior that characterizes the large dielectric permittivity [3]. The new tricritical point we found has a low pressure of ~145 MPa and is close to the Curie temperature of ~395 K, which significantly differs from points found before: 3.4 GPa, 291 K [4]; 6.5 GPa, 130 K [5]. Furthermore, we established that the pressure parameter has a threshold character and can destroy the ferroelectric phase. Critical pressure values depend on the quenching depth and influence the time of domain structure relaxation to the state of thermodynamic equilibrium. Our results demonstrate that the pressure effect upon phase transition can be used to obtain both homogenous and polydomain structures. It is expected that the proposed method will be promising for creating the perovskite solar cells, high-sensitivity thermal sensors, and enhancing energy storage.

REFERENCES


Modeling of Radial Distribution Functions of Liquid Argon Film Confined Between Diamond Surfaces

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Abstract #TM-0169

The one of main structural characteristics of liquids is the radial distribution function; it specifies the change in the number of atoms in the liquid (or density) depending on the distance from the center of a given atom. Note that in a liquid, for any particular atom at a given moment of time, such a distribution of neighbors will be somehow different. However, after averaging over all "central" atoms (or around one atom, but over a long time), a function is obtained that carries information about the characteristic mutual arrangement of atoms in space for a given system. We can say that it characterizes the "probability" of finding an atom at a defined distance from a given atom. There is a clear peak corresponding to the nearest neighbors, and subsequent damped oscillations, which is typical for all simple liquids. Liquid argon was one of the first objects of application of the molecular dynamics method in statistical physics. The interaction of argon atoms is well described by the Lennard-Jones potential.

A computer simulation using the molecular dynamics method of an ultrafine layer of liquid argon enclosed between absolutely rigid diamond surfaces has been carried out. The degree of ordering of the arrangement of liquid molecules is characterized by the radial distribution function therefore the radial load distribution and distribution functions for a film are calculated. The near order is present in liquid Ar, since the probability of detecting molecules (maxima of radial distribution function) at distances corresponding to nearest neighbors is greater than at larger distances. With an increase in the load on the substrate, fluctuations of radial distribution function increase, and the liquid argon molecules stick together, and the film turns into a solid state. When a liquid transforms into a solid state, entropy and internal energy decrease. The average values of the potential and kinetic energy of particles in a liquid are close in magnitude, and the energy of intermolecular interaction is of the same order as in a solid.

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REFERENCES

Piezoelectric Properties and Electron-Phonon Interaction in Semiconductor Arsenide GaAs/AlAs Nanosystems of Plane Symmetry

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Abstract ID #TM-0188

The theoretical studies and application of multilayer resonance tunneling structures are inextricably linked with technological progress in the practical implementation of quantum cascade lasers and detectors [1, 2]. For resonant tunneling structures of the AlAs/GaAs type, the theory of the piezoelectric effect exists only for nanosystems with one isolated potential well. It should also be noted that in this paper [3], it was assumed that the crystal structure of the semiconductor materials of the nanosystem is of zinc blende type, while aspects of the electron-phonon interaction were also not considered. In modern AlAs/GaAs-based nanodevices, semiconductors with a wurtzite-type structure are used; taking into account this fact, adjustments should be made to the form of the initial equations that determine the piezoelectric effect.

Being compared to nitrides, in which the piezoelectric effect leads to the appearance of strong electric fields, arsenide semiconductors do not exhibit pronounced anisotropic properties, being, in fact, homogeneous semiconductor media. Herewith, we report a theoretical study of the piezoelectric effect in the AlAs/GaAs nanosystem [4] using the perturbation theory, restricting ourselves to the first-order approximation in specific calculations. The developed theory allows for an accurate description of the piezoelectric effect, which is observed in semiconductor resonant-tunneling structures based on arsenide semiconductor compounds. Analytical expressions are obtained for the solutions of the Poisson equation, which define the components of the piezoelectric potential, which, in turn, is determined by the displacement components of the nanosystem medium - different types of acoustic phonons. On the basis of Green's function method, the electron-phonon interaction at T=0K and T=100K were investigated. The calculations of the modeling dependencies for piezoelectric potential components and the renormalized electronic spectrum as functions of the geometric design of the nanosystem under study were performed.

We performed calculations of the electron spectrum and quantum transitions between the levels of this spectrum, changed by the influence of phonons, basis on the parameters of a separate cascade of a quantum cascade laser, which were investigated experimentally [5]. It has been established that the electron-phonon interaction leads to a decrease in the energy of quantum transitions by changing the position of the absorption zone. In this regard, we expect that the theory developed by us and the performed calculations will make it possible to directly optimize the efficiency of quantum cascade lasers and detectors, allowing us to make corrections to the energies of working quantum transitions, thus ensuring the stability of the coherent electron tunneling regime.

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Conference Track: “Theory & Modeling”
Molecular Dynamics Study of Graphene-induced Structural Transformation in Ni Surface Layers

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Abstract ID #TM-0204

Graphene is a promising material for application in solar energy, because it has a unique set of properties (such as transparency, high conductivity and good mechanical properties). Thus, the research of graphene interaction with the metals is interesting. In our previous works, we have studied the system "bcc Fe / Graphene" [1], "hcp Ti / Graphene" and "fcc Pt / Graphene". In this work we performed the research of the system "fcc Ni / Graphene". Graphene is used in the form of a monoatomic layer and in the form of nanoplatelets.

Processes of structural transformation in the surface layers of Ni under the influence of a free surface and graphene was the object of our theoretical study. LAMMPS software [2] was used for molecular dynamics (MD) simulation. Model of Ni monocrystal with different crystallographic orientations (001), (011), (111) of free surface was created for MD simulation. This model has been simulated before and after the graphene coating for temperatures 300K and 400K.

Following parameters were calculated:
– complete, kinetic and potential energy systems;
– change of interplanar distances along the normal direction to the surface;
– distribution of metal and carbon atoms;
– layer-by-layer functions of radial atomic distribution;
– general and axial stresses.

An atomic distribution map in the Ni / Graphene system for carbon atoms and the first nickel layer of different crystallographic orientations (001), (011), (111) are constructed.

Comparison of the results for other studied systems were conducted [3, 4]. Based on the comparison of the obtained simulation results for all studied systems, a number of criteria are recommended to ensure satisfactory structural and thermal stability in Metal / Graphene interface for further practical use in solar energy industry.

ACKNOWLEDGMENTS

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REFERENCES

Computational Studies of Atomic and Electronic Structures of Crystal-Glass Composite Materials Based on Phosphate and Borate Glasses

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The study of the atomic and electronic structures of novel glass and crystal-glass composites is an actual research problem [1, 2]. When the surfaces of the components of heterostructural composite materials of different chemical compositions interact, the atoms of the components may mutually diffuse to a certain depth of their volumes. As a result, interface (interphases) layers are formed - transitional regions with unique physical properties, where atoms of both components of the material are present. The physical characteristics of such interface layers are very difficult to predict using only general ideas about atoms, ions or molecules interactions. However, the mutual diffusion of component atoms can be effectively modeled in calculations using the molecular dynamics (MD) methods. Further application of the electronic structure calculation methods to the obtained atomic structures allows to obtain the most relevant micro- and macro-characteristics of the interface layers, in particular, the energy and spatial electronic structures, optical constants, spectra of optical absorption, electronic conductivity, etc.

Computational studies of the atomic and electronic structures of glasses and crystal-glass interfaces were carried out using computational programs of Materials Studio 2019 software package [3]. Three types of composites were considered: a) KBi(MoO$_3$)$_2$ crystal – K$_2$O-P$_2$O$_5$-MoO$_3$-Bi$_2$O$_3$ glass; b) K$_2$Eu(PO$_4$)(WO$_4$) crystal – K$_2$O-P$_2$O$_5$-WO$_3$-VO$_5$ glass; c) LaVO$_4$ crystal – Bi$_2$O$_3$-V$_2$O$_5$ glass. The atomic structures of glasses and interfaces were calculated by MD methods implemented in Amorphous Cell and Forcite programs. The calculations were performed for ~20x20x45 Å three-dimensional periodic cells, which contained 300-500 atoms of composites. The electronic structure calculations were performed in the DFT approximation using the band-periodic plane wave pseudopotential method CASTEP, for which the cells of smaller sizes were used. The partial densities of states, spatial distributions of electron densities were calculated with use of GGA-PBE exchange-correlation functional. Calculations of the excited electronic states energies and optical absorption spectra of particular oxyanianionic molecular groups of interface regions were performed by the TD-DFT method with use of Gaussian program.

The key structure–properties relations in studied glasses and crystal-glass composites are clarified, in particular, dependence of the optical characteristics of composite materials on atomic and electronic structures of interface (interphase) layers. Possibility of “engineering” the corresponding properties of a number of novel composite materials is analyzed.

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The calculations were performed using Bem supercomputer of Wroclaw Center for Networking and Supercomputing (grant no. 488).

REFERENCES


Investigation of Transient Boiling Regime of Water and Nanofluids Heated to Saturation Temperature Using CFD Simulation (ANSYS Fluent)

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Abstract ID #TM-0254

The complex process of convective heat exchange between a solid body and a liquid during its boiling is significantly complicated by the presence of the vapor phase with simultaneous processes of evaporation and condensation. In addition, the presence of steam bubbles that move upward due to the forces of Archimedes leads to an increase in heat dissipation from the heated body. These phenomena cause new boiling conditions that occur quickly and are difficult to model. In this work, a computer simulation of the processes was performed to reproduce and explain the obtained experimental data. The nanofluid was modeled by modifying the physical properties of distilled water, calculated using the empirical formulas. The ANSYS Fluent software package was used for this study.

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REFERENCES

Polarization Phases in a Strained Ferroelectric Nanowire

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Abstract ID #TM-0283

We performed the theoretical study of emerging polarization states in a one-dimensional strained ferroelectric nanowire. Our results demonstrate the existence of non-uniform polar textures, namely, vortex and chiral helical states, which arise due to electrostatic confinement and corresponding depolarization effects. We study how these novel phases appear in a model PbTiO3 nanowire and show the possibility of manipulating and switching these states by temperature and compressive/tensile strains.

To construct the strain-temperature phase diagram [1], we combine the analytical approach with two simulation techniques: phase-field numerical calculations employing the Ginzburg-Landau-Devonshire functional and atomistic simulations. We reveal three distinct polar phases: vortex state with polarization swirling around the wire axis; uniform polarization state extending along the wire axis; and the helical state, which mediates the vortex and uniform phases, with polarization screwing along the wire axis. We calculate the chirality density of the helical phase as a function of strain and temperature; this new functionality of one-dimensional ferroelectrics is of special interest for applications, including optoelectronics, quantum communication technologies, and neuromorphic computing [2, 3].

ACKNOWLEDGMENTS

Work performed with co-authors in Ref. [1]. This work was supported by the Alexander von Humboldt Foundation and by the related projects listed in Ref. [1].

REFERENCES


Electromigration Effects in Processes of Nano-Structured Thin Films Growth

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Abstract ID #TM-0395

We discuss effects of electromigration in processes of nano-structured thin films growth at condensation from gaseous phase and epitaxial growth in the framework of numerical simulations. It will be shown that an increase in the strength of the electric field applied to the substrate promotes formation of percolating structures of adsorbate. We will analyze dynamics of the surface morphology change in details. This study provides insight into details of electromigration effects at self-organization of adatoms into percolating adsorbate islands during nano-structured thin films growth at both condensation from the gaseous phase and epitaxial growth of multi-layer pyramidal-like adsorbate structures.
Phase Field Modeling Radiation Induced Precipitation in Diluted Zr-alloys

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Abstract ID #TM-0396

We study nano-sized precipitates formation in diluted Zr alloys under neutron irradiation by using phase field modeling. It is shown that in a sample containing pre-existent precipitates of secondary phase irradiation results in dissolution of precipitates at small doses and re-precipitation with dose accumulation. By considering extremely diluted alloy it is found that radiation induced precipitation begins after incubation dose due to combined effect of radiation enhanced diffusion and ballistic mixing. Statistical analysis for precipitate size, their number density and size distributions is provided. Obtained data are compared with experimental observations.
TRACK 13
“INTERDISCIPLINARY & MISCELLANEOUS TOPICS”
Large Area Fabrication of Bio-sourced Polymer Nanofibers for Food Packaging Applications

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Abstract ID #IMT-0075

Nanofiber and microfiber mats of edible or bio-sourced polymers are promising materials for advanced food packaging applications [1-3]. In this study we compare electrospinning of two bio-sourced polymers, suitable for edible food packaging applications: pullulan, as well as chitosan. Pullulan was dispersed together with cyclodextrin in a solution of limonen-cyclodextrin (aq) and chitosan was dispersed together with gelatin in acetic acid (aq). Dynamic viscosities were measured and adjusted for electrospinning. Fiber mats were then produced by electrospinning at high voltage (between 15 kV and 21 kV) for electrode distances of 10 - 12 cm. The fiber shape and dimensions were measured using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fiber diameters were investigated as a function of process parameters; typical fiber diameters of 320 nm and 150 nm were obtained for pullulan and chitosan fibers, respectively. We have successfully produced large area fiber mats using an electrospinning pilot production system (home-built) using a rotating cylindrical collector electrode. The obtained large area fiber mats and our constructed pilot production system are promising for the development of edible, bio-sourced packaging applications.

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Composite Electrospun Polymer Fibers for Improving Heat Transfer Systems

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Abstract ID #IMT-0080

Heat transfer in polymer-based systems is limited due to their intrinsic low thermal conductivity. However, the addition of thermally conductive fillers to the polymer matrices can increase their thermal conductivity. Nonetheless, poor processability and inferior mechanical properties are still limiting factors as they depend on the concentration and dispersion of filler in the composites [1]. One of the most versatile methods to produce polymer meshes and membranes is electrospinning which allows producing composite fibers in one-step manufacturing. It is also an effective method for improving the dispersion of fillers even in high concentration and directional arrangement of fillers along the polymer fibers, which is one of the major challenges in fabricating thermally conductive nanocomposites. Besides, the fillers' organization during electrospinning directly affects the polymer chains' alignment and reorientation [2], which increases the thermal conductivity and mechanical performance of produced fibers [3].

In this study, ceramic nanoparticles such as boron nitride (BN) and silicon nitride (SiN) are used to fabricate electrospun composite fibers. The role of concentrations, distribution, and size of nanoparticles on the thermal conductivity and mechanical tensile strength have been investigated. The optimized blend and co-axial electrospinning have been performed to produce the improved mechanical and thermal properties of electrospun fibers and membranes. The obtained results show the promising application in the temperature control system for many electronic devices. This study also extends the theoretical knowledge and understanding of the thermal conductivity and heat transfer at the nanoscale in the polymer-ceramic composite.

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REFERENCES


Features of Phase Formation in the Structure of Experimental Low Cost Titanium Alloys

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Abstract ID #IMT-0099

Tanium alloys are widely used in various branches of modern industry. One of the promising areas at present is the development and production of low cost titanium alloys. The production of such alloys is carried out primarily for their use in the aerospace, chemical, energy, engineering, military and medical industries. The urgent task is to study the effect of alloying on structural-phase composition and phase-forming processes of titanium alloys [1-4]. This allows us to assess the impact of these processes on the properties of the metal at the structural level.

The paper presents a study of experimental low cost titanium alloys of different alloying systems, obtained by electron beam melting: Ti-1,5Fe-0,4O (alloy 1) and Ti-2,8Al-5,1Mo-4,9Fe (alloy 2). Studies by X-ray diffraction analysis have shown that the low cost titanium alloy Ti-2,8Al-5,1Mo-4,9Fe is a two-phase pseudo-β alloy. It consists of beta-phase titanium (β-Ti) in the amount of 89.02% (lattice parameters a = 2.9400, c = 4.6700) and alpha-phase titanium (α-Ti) in the amount of 10.98% a = 3.2225). Titanium alloy Ti-1,5Fe-O is a two-phase pseudo-α titanium alloy in which the share of alpha-phase (α -Ti) is 90.42% (lattice parameters a = 2.9501 c = 4.6785) and beta-phase (β-Ti) - 9.58% (lattice parameters a = 3.2137). Transmission electron microscopy was used to study the phase components, their substructure and parameters, dislocation structure and features of phase formation in the studied experimental alloys. The stoichiometric composition of dispersed phase separations in the internal volumes of the alloy structure, which differ in alloying systems, was studied in detail with the help of TEM microdiffraction patterns.

Studies have shown that in the structure of the titanium alloy Ti-2,8Al-5,1Mo-4,9Fe there are dispersed intermetallic nanoparticles different in morphology and stoichiometric composition. These are the phases: TiAl with a size of 10…110 nm; Fe₃Ti - 10…40 nm and Mo₅Ti₄ - 20…120 nm. Studies of the structure of the titanium alloy Ti-1,5Fe-O showed the presence of mainly nanoparticles of oxides: Ti₃O₅ size 10…80 nm and TiFeO₄, FeTiO₃ size 70…210 nm and intermetallics Fe₃Ti size 10…40 nm. It is shown that the fine-plate structure of the investigated experimental low cost titanium alloys is characterized by the formation of nanoparticles of intermetallic and oxide phases with uniform dislocation density distribution.

REFERENCES

Structure Features of the Surface of Structural Alloyed Steel after Pulse-Plasma Treatment

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Abstract ID #IMT-0121

Nowadays, the modern industry pays special attention to the issues of increasing the reliability, efficiency, and service life of manufactured machines and units. Solving these issues requires the use of materials that can work in various conditions in which mechanical wear occurs. Therefore, it is essential to ensure the durability of machine parts and mechanisms, which stimulates the development of new, highly efficient resource-saving technologies [1]. These technologies are also aimed at increasing the wear resistance of the working surfaces of the materials from which they are made.

The paper presents the results of a study of the development of one of the technological modes of pulse-plasma treatment of structural alloyed steel 40X (0.36…0.44 C%; 0.17…0.37% Si; 0.5…0.8% Mn; 0.3% Cu; ≤ 0.3% Ni; 0.8…1.1 Cr %; ≤ 0.3%Cu). Steel 40X is widely used in mechanical engineering in the production of high-strength parts. After quenching and tempering, this steel has high mechanical properties: σ0,2=720…1560 MPa; σB=860…1760 MPa; δ ≥ 8%; ψ ≥ 35%. In this experiment, steel 40X was used after preliminary heat treatment (isothermal quenching for bainite in oil at T=850°C). The subsequent pulse-plasma treatment was carried out at a specific heat flux Q=6.5×108 W/m². A complex of methods for studying samples of 40X steel, including optical metallography, scanning electron analytical microscopy, and transmission electron microscopy, showed the following. The base metal is represented by the structure of upper and lower bainite with a small amount of martensite. Base metal microhardness is 4120…5090 MPa. As a result of pulse-plasma treatment of the surface of 40X steel, a layer with a dispersed martensitic structure is formed on the metal surface to a depth of 70 µm during the formation of a substructural component. The microhardness of this layer is 6550…5160 MPa. The parameters of the substructure directly in the surface layer along with the depth of the metal up to 20 µm are 30…120 nm. Further, at a depth of 25…60 µm, a substructure of 50…230 nm in size is formed. A uniform distribution of dislocation density is observed in the forming substructure (r ~ (2…3) 1011cm⁻²). The absence of dislocation density gradients predetermines the lack of local internal stress gradients. This will provide crack resistance to the treated surface in this zone. Industrial tests of 40X steel samples treated by the plasma-detonation method confirm a significant improvement in the tribological properties of products. Hardening leads to a decrease in the wear rate of samples by 1.2…3.7 times (oil lubrication) and 1.4…4.3 times (emulsion lubrication) when tested on an end-face friction machine. When tested on a reverse friction machine (lubricated with an emulsion), the wear rate of the samples is reduced by 1.8…3 times.

REFERENCES

Effect of Surface Mechanical Pulse Treatment on Nanocrystallization and Properties of Structural Steels

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Abstract ID #IMT-0158

Surface nanocrystallization of the structural steels is becoming increasingly effective technique for improvement of the mechanical properties and protection of the metal surface of engineering components. Grain refinement in the surface layer leading to formation of nanocrystalline material is commonly induced by severe plastic deformation using different surface mechanical attrition treatment methods [1–4].

One of the methods enabling formation of surface layers with nanocrystalline structure (NCS) on carbon and low-alloyed steels is surface mechanical pulse treatment (MPT) [3] involving fast heating, severe plastic deformation and rapid cooling of local areas of the treated surface layer. It is based on high-speed friction which leads to heating of the treated metal surface in the friction contact zone to temperature above the temperature of structural-phase transformation (~ 1000 °C) and rapid cooling by supplied technological fluid (TF). Depending on the applied TF, alloying of the surface nanocrystalline layer of the treated steel by components of TF occurs during MPT. Therefore, MPT combines grain refinement to the nano scale, quenching and alloying of the surface metal layer [3].

The present paper aims to analyze the influence of some factors, namely, force regime and parameters of MPT, type of TF, and preliminary heat treatment on the surface NCS formation on carbon, low-alloyed and alloyed steels by MPT, thermal stability of the surface NCS and their effect on mechanical properties, namely, microhardness, wear resistance, fatigue and corrosion fatigue strength, and contact fatigue resistance.

The formation of surface nanocrystalline structure on structural steels using mechanical pulse treatment technique was analysed. Surface layers with gradient NCS were formed by MPT on carbon, low-alloyed and alloyed steels. The key factors controlling grain refinement were considered.

Surface nanocrystalline layers with grain size in the range of 12–60 nm on the surface were fabricated depending on the technological parameters of mechanical pulse treatment and type of the TF. Grain size of NCS was depended on treatment regime of MPT (specific pressure in the friction contact zone, rotational speed of specimen, longitudinal feed of strengthening tool, and rotational frequency of treated specimen) and type of cooling TF which directly influenced on microhardness of the surface: it increased due to decreasing in grain size.

Surface NSC formed on low-alloyed pearlitic steels by MPT were characterised by thermal stability up to 500 °C. Structural steels with the surface nanocrystalline structure were characterised by improved mechanical properties, namely, microhardness, wear resistance, fatigue and corrosion fatigue strength, and contact fatigue resistance.

REFERENCES

Development of Biopolymer Packaging Films and Technology of their Ultrasonic Welding

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Abstract ID #IMT-0224

Biopolymer that occupies a significant place in industrial production – polyhydroxybutyrate (PHB) – a biopolymer that is physically similar to polystyrene, found in the bacterium Alcaligepes eutropus. PHB is rapidly destroyed by soil microorganisms. The polymer is obtained by growing Azotobacter on glucose with oxygen limitation, as well as Alcaligenes- with nitrogen deficiency in a biologically active environment. The weldability of biodegradable polymer films intended for food packaging and manufactured in the laboratory on the basis of PHB was investigated experimentally. A very important factor of a proper polymer weld joint is its mechanical properties and structure at the molecular level, resulting in similar or different properties of the joint and base material.

A film designed for food packaging and made in the laboratory from a mixture of PHB and bioplasticizer was used. Biodegradable film from a mixture of PHB polymers was welded by ultrasound on a standard Branson press type installation. A sonotrode with a flat horizontal surface of two types was used - a flat polished surface and a profiled surface with regular pyramidal protrusions of the “knurling” type. During the heating, the working pressure was 0.3 MPa.

The biodegradable filler seams welded with a flat-surfaced sonotorod were well-formed, but the heating of the material was somewhat uneven over the joint area. Small splashes of molten material from the welding zone were observed at some seams. The overburden seams of the biodegradable film, welded with profiled sonotorod, were formed with the formation of uniform penetration over the entire joint area. On the outer surface of the weld, there are small fragments of destructed polymer material, which are formed due to the concentration of mechanical stresses and temperature increase at the peak protrusions of the profiled surface of the sonotrode.

In order to examine materials' properties, mechanical tests were performed. All overhead welds of ultradegradable biodegradable films were destroyed by the main material during tensile tests. Nanoscale characterization was performed by means of X-ray diffraction, FT-IR spectroscopy and surface analysis using scanning electron microscopy. Performed studies allow determining structural differences across welded joints, which results in different mechanical properties.

REFERENCES


Conference Track: “Interdisciplinary & Miscellaneous Topics” 13imt-6
When May Storage of Nanoparticles of Noble Metals Cause Changes in their Properties?

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Abstract ID #IMT-0230

Nanoparticles of noble metals (namely, gold, silver, or bimetallic) are one of the most widely used nanomaterials in the world. There are lots of methods for their synthesis, stabilization, and functionalization, therefore, gold and silver nanoparticles can be found using for electronics, solar energy, biosensors, nanocatalysis, drug delivery, etc [1-3]. However, the physical and chemical properties of colloids of nanoparticles depend much on their stability. Namely, prolonged stability of the colloidal solution of nanoparticles is one of the main tasks for their synthesis.

Unfortunately, the dependence of the stability of the nanoparticles on the storage conditions has not been studied in detail yet. As a consequence, we may find out in papers some information regarding the non-reproducibility of some experimental results with gold or silver nanoparticles. In the work using LDVO theory [4] with size-dependent Hamaker constant [5] for nanoparticles, it has been theoretically shown, that in some cases the nanoparticles may aggregate on the inner surface of the storage glassware. This aggregation may cause changes in the concentration of nanoparticles in the solution, and consequently changes in their physical properties, and chemical and biological activity. Two parameters were taken into account: the temperature of storage and the material of the glassware. Theoretical considerations were checked by testing the antimicrobial activity of silver nanoparticles for different storage conditions and supported by measurements of optical absorbance spectra.

Based on theoretical and experimental results obtained, recommendations for storage conditions of nanoparticles of noble metals were constructed. We recommend storing colloids of nanoparticles at nearly room temperature in plastic glassware.

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REFERENCES

Effect of Low-Temperature Aging on Mechanical Behavior of Metastable β-type Ti-Mo-Sn Alloys

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Abstract ID #IMT-0266

Titanium-based alloys have a great future due to their unique specific mechanical, and corrosion properties, including good biocompatibility. Metastable β-Ti-Mo alloys demonstrate several reversible and irreversible deformation mechanisms: stress-induced (β→α"), martensite transformation, mechanical twinning, and dislocation slip [1-3]. They are deformed by the mechanisms of Transformation-Induced Plasticity (TRIP) and Twinning-Induced Plasticity (TWIP) and have several advantages: a high strain hardening rate and a high uniform elongation. Metastable β-phase Ti alloys are used in structural applications where high specific strengths, low elastic modulus, good fatigue resistance, sufficient toughness, excellent corrosion resistance, and good formability are required and possess excellent biocompatibility leading to their use in implants.

The paper considers in detail the structural deformation behavior of ternary metastable β-type Ti-Mo-Sn alloys subjected to complex thermomechanical treatment under different loading conditions, including mechanical cycling, which indicates the complex nature of deformation with the prevalence of TRIP/TWIP mechanisms. To obtain nanocomposite structure, the homogenized ternary Ti-Mo-Sn alloys with 10, 12, 14%Mo and 1, 2, 4, 6, 8 % Sn (wt.) were quenched in water from 1173 K, then annealed (or aged) at low temperatures 373 and 473 K for 60 s for nanoparticles precipitation formation in an alloy's matrix. The optimal combination of mechanical properties under uniaxial tension corresponds to an alloy Ti-12Mo-4Sn (wt.%) after annealing at 473K for 60 s, for which the maximum yield strength σy=680 MPa and ultimate tensile strength σut=1125 MPa with sufficiently high plasticity of 42% and Young's modulus were achieved after aging at 473K for 60 s. The mechanical characteristics of this alloy make it potentially suitable for commercial biomedical applications.

In the context of gaining mechanical properties, it is worth highlighting the record rates of strain hardening, especially for compositions Ti-10Mo-(2÷6)Sn (wt.%). The prevailing mechanism of the deformation according to XRD analysis of these alloys is the TRIP effect, which much exceeds the TWIP effect concerning the alloys with higher content of Mo and Sn. It should be noted that aging plays a huge role in changing the mechanical parameters of Ti-Mo-Sn alloys, which is accompanied by the release of nanosized particles of the β-phase [4]. Low-temperature aging of Ti-(10,14)Mo-(2÷6)Sn (wt.%) alloys contributes to a significant increase in strength up to 1.5-2 times with a slight loss of plasticity due to the nanocomposite structure, where precipitation of β-phase nanoparticles coherently bonded to the matrix. The phase morphology and relative volume fraction of each phase depend on the composition of the alloy and thermo-mechanical processing.

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Conference Track: “Interdisciplinary & Miscellaneous Topics” 13imt-8
Research of Influence of Technological Parameters on Morphological Features of Slawsonite Ceramics

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Abstract ID #IMT-0279

The development of new generations of guided missiles and anti-aircraft missile systems requires scientists to develop and implement a wide range of materials with high physical and chemical, mechanical, thermal and electrophysical characteristics. Therefore, the creation of new ceramic materials based on the crystalline phase of slawsonite SrAl$_2$Si$_2$O$_8$, on the basis of which radio-transparent fairings are obtained, is an urgent problem of modern materials science. The influence of technological parameters on the properties of slawsonite ceramics is investigated in the article. The synthesis of the slawsonite phase was carried out using technical raw materials: alumina, strontium carbonate and quartz sand. Variable technological factors were: firing temperature – 1350 °C and 1400 °C, holding at maximum temperature – 2 and 4 hours. Morphology and phase features of the obtained samples were studied by X-ray phase analysis and scanning electron microscopy. Regularities of change of physical and mechanical properties depending on temperature and duration of firing of experimental ceramics are established. It is proved that with increasing the firing time of the samples the values of water absorption and open porosity decrease and the apparent density of slawsonite ceramics increases. The mechanical and dielectric properties of experimental ceramics were experimentally studied, the values of which are in the ranges $5.8 \div 13.2; \sigma \sim 140 \div 390$ MPa. According to the values of the dielectric constant ($\varepsilon = 5.8$) at a firing temperature of 1350 °C and holding for 4 hours, the prototypes meet the requirements for radio-transparent materials.
Green Synthesis of Magnetite Nanoparticles Using Hydrothermal Method for its Potential Antibacterial Application in Disease Management of Agricultural Crops

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Abstract ID #IMT-0332

Nanotechnology has gained much attention for its potential bio-applications in medical science [1]. Nanoparticles, which are one of the main components of nanotechnology, have been used in a wide range of applications due to their unique properties [2]. Magnetite (Fe3O4) nanoparticles are widely used in various applications due to their unique properties such as high magnetic susceptibility, chemical stability, and toxicity [3]. This study aims to explore the antibacterial and antifungal properties of iron oxide nanoparticles synthesized by chemical as well as green route using hydrothermal method. In this respect, the iron oxide (Fe3O4) NPs nanoparticles were prepared synthesized using ferric chloride as a precursor, sodium acetate as precipitating agent [5] and the bark extract of Neem Tree (Azadiractha indica) bark extract as a green source. The Nanoparticles (NPs) obtained by chemical and green synthesis as well were characterized by UV-visible spectroscopy, Transmission Electron Microscopy (TEM), and X-ray Diffraction (XRD) and Dynamic Light Scattering (DLS). The average particle size of synthesized NPs was found to be ~ (15-20) nm which commensurate well with DLS studies. UV-visible spectra of iron oxide NPs show absorbance in visible range. Further, the antimicrobial activities of synthesized iron oxide nanoparticles were evaluated by using agar well diffusion method against phytopathogens such as Xanthomonas campestris pv. campestris, Bacillus subtilis and pseudomonas fluorescence and mycopathogens such as Fusarium oxysporum, and Phytophthora by poison food agar assay. The outcome of this study will be very useful for its potential application in the management of bacterial and fungal plant pathogens during crop cultivation in agriculture.

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REFERENCES

Polidiacetylenes – Thermochromic Indicators for Potential Application in the Food Industry

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In recent years, dynamic development of the packaging industry has been observed, related to technological advances in the field of material engineering. Currently, there is an attempt to develop the so-called intelligent packaging. These packages, in addition to traditional functions such as protection against damage and external factors, also have a monitoring and informative function. This is possible thanks to the placement of appropriate interactive indicators on them, which can monitor various parameters, e.g. the ambient temperature of the products. The information about temperature fluctuations seems to be especially useful for frozen foods stored at -18°C. Increasing the storage temperature may defrost them and cause spoilage.

Potential compounds that can be used in intelligent packaging are polydiacetylenes (PDAs), which are an object of increasing interest all over the world. These compounds, in response to various external stimuli, such as temperature, pH, solvents, metal ions, microorganisms, or biomolecules, may undergo polymerization accompanied by a change in their chromatic and fluorescent properties [1, 2]. Such properties make it possible to classify PDA into the group of sensory materials [3]. Due to the properties of this group of compounds, they can be used as potential bio- or chemosensors.

The presented research includes the synthesis of the PDA series, showing color change under the influence of temperature. The structures of the obtained compounds were confirmed by spectroscopic methods. Moreover, the transformation temperatures of the compounds were determined by means of UV-DSC.

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REFERENCES

Leuco Dye-Based Thermochromic Systems for Application in Temperature Sensing

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Leuco dye-based thermochromic systems are classified as intelligent materials because they exhibit thermally induced color changes. Thanks to this feature, they are mainly used as temperature indicators in many industrial sectors. For example, placing a thermochromic material on a chemical reactor may warn about exceeding the maximum permitted temperature for a chemical process. Usually two components, a color former and a developer are needed to produce a system with irreversible color change. The color former is an electron donating (proton accepting) compound such as fluoran leuco dye. The developer is an electron accepting (proton donating) compound such as organic carboxylic acid. When the developer melts, the color former - developer complex is created and the thermochromic system becomes colored. Typically, the melting point of the applied developer determines the temperature at which the color change occurs. When the lactone ring of the color former is closed, then the dye is in its colorless state. The ring opening, induced by the addition of a proton, causes the dye to turn into its colored state. Since the color former and the developer are often solid, they can be incorporated into polymer films to facilitate their practical use in industry.

The objective of this research was to fabricate a leuco dye-based thermochromic system that will irreversibly change color after reaching the temperature of 100 °C. For this purpose, benzofluoran leuco dye (as color former) and phenoxyacetic acid (as developer with a melting point of 100 °C) were introduced into the polymer films during the drop casting process. The film preparation process was optimized in order to obtain thin films with appropriate properties such as transparency, flexibility and homogeneity. Among the optimized factors were the concentration of benzofluoran leuco dye and phenoxyacetic acid, the type, average molecular weight and concentration of the polymer, and the type and concentration of the surfactant. The selected films, containing benzofluoran leuco dye and phenoxyacetic acid, were combined by mild heat treatment. Structural characterization of single and combined films was carried out by FTIR spectroscopy, morphological analysis was performed by optical microscopy and SEM, phase transitions were examined by DSC, color changes were investigated by digital photography and UV-Vis spectroscopy, while emission changes were studied by photoluminescence spectroscopy.

The resulting thermochromic system is colorless at room temperature, but after reaching 100°C the developer melts and it turns irreversibly pink. Therefore, it can be used together with electronic temperature indicators to warn against water boiling in cooling systems.

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Sol-gel and Polymer Thin Films as Potential Candidates for Application in Planar Photonics Systems

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Thin films prepared from sol-gel and polymeric materials are great candidates for application in planar photonic systems. By the proper selection of materials and preparation protocol, preparation of films with designed properties such as refractive index and thickness is possible. Moreover, their additional advantages are low cost, facile fabrication and easy processing. They may find application as planar waveguides [1-3] or, when activated with organic luminescent dyes, as light amplification media [4]. However, the preparation conditions such as withdrawal speed (when using dip-coating technique) or heat treatment conditions must be optimized in order to achieve films with desired properties.

We report fabrication of thin films based on SiO$_2$ or organically modified SiO$_2$ (ORMOSIL) and TiO$_2$. Moreover, sol-gel films activated with luminescent dye (Rhodamine B) were prepared. Fabrication of polymeric films was discussed as well. Influence of different preparation conditions on optical properties of sol-gel films and Rhodamine B activated films was studied. The refractive index and thickness of the films were evaluated using ellipsometry or profilometry. It was found that they could be controlled by adjusting the relative amount of SiO$_2$ and TiO$_2$ precursor, heat treatment conditions and withdrawal speed. Sol-gel films activated with Rhodamine B were characterized using absorption and emission spectroscopy. The optical transmission losses of selected planar waveguides were determined using scattered-light method. Moreover, simple approach of fabrication of the periodic structures in ORMOSIL based and polymeric thin films using nanoimprint technique was implemented.

By proper selection of materials and preparation protocol, thin waveguiding film with implemented grating coupler and low transmission losses was obtained.

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Organic Dyes as Potential Activators for Photonics/Nanophotonics Applications – Case Studies

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Today’s technology and photonics are based on newer and newer organic dyes with high luminescent properties. However, together with good optical properties, these dyes must also be chemically and thermally stable, especially as they often are incorporated into sol-gel matrices during the preparation of hybrid platforms. This study presents two case studies on the doping of SiO₂ materials synthesized by the sol-gel method with xanthene dyes. The first case is new long-chain compounds - xanthene derivatives and their spectroscopic and chemical properties [1-2]. On the other hand, hybrid materials doped with commercially available xanthene dyes and their spectroscopic properties are dependent on temperature [3].

When considering potential applications, and thus when designing materials with a strictly defined emission spectrum, the tautomerization and prototropism of given dyes are particularly problematic. We show the possibility of doping the SiO₂-based layers with a newly synthesized methylated derivative. To obtain organic-inorganic hybrids, different pH catalysts were used to synthesize the sol-gel silica network, which resulted in different emission colors under the UV lamp after gelation, most likely due to the different forms trapped in the matrix. We also show the possibility of designing the spectral range of emissions using annealing materials based on xanthene dyes available on the market. The research also shows the possibility of applying synthesized layers on a microscale using spin or dip coating.

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Correlation Between the Synthesis Route and Spectroscopic Properties in Nano and Micro-Crystalline Yb$^{3+}$-Doped LuPO$_4$

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Rare earth-doped orthophosphates establish a considerable family of compounds characterized by different physico-chemical properties. Their high thermal stability, high insolubility, relatively cheap synthesis, and the fact that they are good host lattices for RE$^{3+}$ ions make them a new promising matrix for inorganic luminescent materials. Among the lanthanides ions, Yb$^{3+}$ is an optically active ion for laser applications but also very often is used as a sensitizer in transfer energy processes. In addition, the possibility to obtain effective luminescence in the NIR region makes it attractive also from the bio-imaging point of view. So far only few papers devoted to the RE$^{3+}$-doped MPO$_4$ compounds reported basic research on influence of synthesis route on structural and spectroscopic properties of obtained materials. However, that type of research is very important for full understanding of the spectroscopic properties and modeling new efficient optical materials with potential applications.

So, taking advantage of Yb$^{3+}$ ion as a structural probe, here we present a detailed analysis of both structural characterization and high-resolution spectroscopic properties of Yb$^{3+}$-doped LuPO$_4$ in the form of nano/micro-crystalline powders crystallizing in a zircon-type tetragonal system. A series of nano-crystalline samples (0.5 – 5 mol%) was obtained by microwave-assisted synthesis. Here, the RE$^{3+}$ nitrates and a task-specific ionic liquid (TSIL), i.e., choline dihydrogen phosphate (as the reactant), and an in-situ nanoparticle templating agent were employed. This protocol allowed to fabrication of fine nano-size powders exhibiting desired well-crystallized single-phase phosphate nano-materials. For comparative study, a series of micro-materials obtained using the high-temperature solid-state reaction was used. The comparison of nano and micro-crystalline materials revealed unexpected properties. Two non-equivalent symmetry sites of Yb$^{3+}$ in LuPO$_4$ host were confirmed. The results were correlated to LuPO$_4$ activated by Nd$^{3+}$ reported by us previously [1-3].

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Un-Expected Dominant Substitution of Ba$^{2+}$ Site Instead of La$^{3+}$ One in Cubic Nd$^{3+}$-Doped BaLaLiWO$_6$ Perovskites – Promising Host Lattice for Transparent Ceramics

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Abstract ID #IMT-0424

Searching new compounds which could be useful for production of new optical transparent ceramics we were interested in perovskite-type tungstates. The AA’BB’O$_6$ perovskites widely examined and applied for practical uses are not known in the form of sintered materials showing transparency. As potential candidates for transparent ceramics should possess highly symmetric crystal systems, BaLaLiWO$_6$ characterized by a cubic structure, seems to be a candidate to realize this very difficult task.

A series of micro-crystalline samples activated by Nd$^{3+}$ ion (0-20 mol%) was synthesized using a high-temperature solid-state reaction. The Nd$^{3+}$ dopant was chosen for two reasons: laser dopant and structural probe. Powder and single crystal X-ray diffraction reflections were indexed to the cubic structure (s. g. Fm-3m). Crystal structure of BaLaLiWO$_6$ has been solved basing on the small single crystal selected from micro-crystalline powder, and has been reported for the first time. The powder diffraction patterns were also refined by the Rietveld method.

The originality of this research results from unexpected substitution of divalent Ba$^{2+}$ ions by small concentrations of trivalent Nd$^{3+}$ ones till 7 mol% of optical activator and above this value the replacement of both Ba$^{2+}$ and La$^{3+}$ sites. Exchange of Ba$^{2+}$ by Nd$^{3+}$ ions leads to the formation of cationic vacancies due to the charge compensation: 3Ba$^{2+}$ → 2Nd$^{3+}$ + □ (vacancy), well-manifested in unit cell expansion. It has also consequences in the spectroscopic properties. Complementary techniques like XRD, SEM combined with low-temperature high-resolution spectroscopic ones helped to elucidate the main features of this promising optical material. A few Nd$^{3+}$ non-equivalent symmetry sites and inhomogeneous Nd$^{3+}$ ion distribution in the lattice, detected by site-selective laser spectroscopy at 77K, have been pointed out in accordance with the crystallographic analysis. The disorder of the structure manifests in broad absorption and emission bands even at low temperature. First translucent microceramics with quite high density were fabricated by Spark Plasma Sintering (SPS) method. Their microstructures and luminescent properties were investigated.

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Preparation and Characteristics of Alginate Membranes Containing Dispersed Nanowires of Nickel and Silver, Used in Ethanol Dehydration in the Pervaporation Process

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Looking for modern and innovative filler materials for membranes, silver (Ag) and nickel (Ni) nanowires were used as a filler for hybrid alginate membranes in the process of ethanol dehydration via pervaporation. The nanowires have the application in electronic, optoelectronic, and nanoelectromechanical devices however, they have not yet been used as fillers of hybrid membranes. The project expected a positive effect of the addition of nanowires to the polymer matrix on the separation process of the water-ethanol mixture due to the elongated shape of the nanowires as well as the magnetic properties of the nickel nanowires. The applied nanowires were synthesized separately by the precipitation method (polyol-Ag and droplet method in the presence of a magnetic Ni-field) and combined with the polymer matrix solution (Ex-situm) in the appropriate proportion. The obtained fillers and membranes were characterized by SEM, and FTIR, measuring the degree of swelling and the contact angle. On the basis of SEM images, it can be noticed that the nanowires are uniformly distribution into polymer matrix. FTIR, the degree of swelling, and contact angle measurements indicated the decrease in hydrophilicity of obtained membranes after addition nanowires. The evaluated parameters describing the effectiveness of pervaporation process i.e. flux, separation factor and pervaporative separation index showed the positive effect of addition of nanowires to alginate matrix on the process of water-ethanol separation. It can be noticed that in relation to the pure alginate membrane it is possible to obtain at least 3 times better separation factor, 10 times better value of pervaporative separation index, and lower by half the value of the total normalized flux.
Nanotechnology of Protein Gel Based on Finely Dispersed Powder from Giant African Land Snail

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Abstract ID #IMT-0452

The global food crisis, which is worsening due to climate change and military actions against agrarian countries such as Ukraine, needs special attention of scientists. The worst food situation is in African countries. High-tech processing of new sources of food raw materials with high nutritional and biological value, economic efficiency and availability for the entire population is the way to overcome hunger. Such food technologies also include extending shelf life, allowing food to be stockpiled before critical periods of food supply, such as winter in agrarian countries and periods of drought in importing countries.

The aim of the study is the nanotechnological processing of the Giant African land snail, which is easy to grow in greenhouses, to obtain finely dispersed powder and protein isolate gel. These products have extended shelf life and high biological value, and are semi-finished products for the production of a wide range of food products rich in complete protein.

The goal is achieved by the production of finely dispersed powder by drying and grinding into flour Giant African land snail (without mucus and shell), land snail flour has a particle size of 5 μm or more. Giant African land snail (Lissachatina fulica) is a species of large land snail that belongs to the subfamily Achatininae of the family Achatinidae.

Giant African land snail flour is subjected to pH-treatment and mild heat treatment to impart colloidal properties, resulting in the formation of a gel with specified functional and technological properties. pH-treatment is a method that unfolds the protein structure in an acid-base environment, which leads to changes in the globular protein (the molten globule effect), which improves the functional properties of proteins. Protein isolate gel has high emulsifying properties, which leads to the formation of a stable fat-in-water phase that does not separate.

Protein isolate gel with high functional-technological properties, such as moisture-retaining, emulsifying, foam-forming and complete protein content up to 95% is good for food industry. This product can be used for vegetarian, military, child and dietary food, and is important for the meat, oil and fat, bakery, confectionery, canning and food concentrate industries. Protein isolate gel is also perfect for use in cooking.

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Nanotechnology, isoprotein, protein, giant snail, vegetarian food, hunger, food crisis, war in Ukraine, climatic changes, combat rations, World Food Programme.

REFERENCES

The National MagLab: An Ecosystem of Innovation and International Science Diplomacy

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Abstract ID #IMT-0453

The National High Magnetic Field Laboratory (MagLab), NSF-supported, has campuses at Florida State University, University of Florida, and Los Alamos National Laboratory. It is the largest and highest-powered magnet laboratory in the world and is unique among US National laboratories in its breadth and depth of research probing basic and applied questions in materials, energy, sustainability, and life. Every year ~2,000 scientists from ~300 countries yielding ~400 peer-reviewed publications make the MagLab an epicenter for international collaboration, even in this changing climate of science diplomacy. I will present an overview of the MagLab facilities, recent records in magnet technology, and some pioneering international collaborative research highlights.
Sorption of Mercury in Batch and Fixed-bed Column System on Nanoporous Hydrochar Obtained from Apple Pomace

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Abstract ID #IMT-0461

This paper presents the methodology for the preparation of hydrochar obtained from waste materials of natural origin and investigates its sorption properties in the batch system and in the flow-through column system [1-3]. The hydrochar material was obtained from apple pomace, which was hydrothermally carbonized in 230°C for 5 h in a hydrothermal reactor. The hydrochar formed in the process was thermally activated with an inert gas flow – CO₂. Obtained materials were characterised with XRD, ATR, SEM EDS and low temperature nitrogen vapor sorption (BET) analyses. The obtained hydrochar was analysed for sorption of mercury ions from aqueous solutions [4, 5]. Equilibrium isotherms (Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Hill, Redlich-Peterson, Sips and Toth) and kinetic models (Pseudo-first order, Pseudo-second order, Elovich and Intraparticle diffusion) were determined [6, 7]. The sorption of mercury ions from an aqueous solution with a concentration of C₀ = 100 mg Hg/dm³ has been carried out in a flow-through column system. The data obtained from adsorption were fitted to mathematical dynamic models (Bohart-Adams, Thomas, Yoon-Nelson, Clark, BDST and Yan) to illustrate the bed breakthrough curves and to determine the characteristic column parameters.

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ABSTRACTS

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