



Plenary Sessions:

PL01

Beyond Adsorption and Because of Adsorption: Exploring the silent aspect of carbon porosity

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Abstract

In this talk we would like to provide an insight into our perspectives on the new applications of nanoporous carbons that were inspired by the graphene features and its presence in these carbonaceous materials. A significant advancement to the “new” science of the “old” nanoporous carbons is in their new application such as gas sensing and ORR and CO₂RR catalysis. In these applications both surface chemistry and porosity are crucial factors determining the specific performance. The mechanism of specific processes based on an involvement of porosity will be proposed.

Our inspiration by the science of graphene combined with the comprehensive knowledge of activated carbons surface chemistry, texture, morphology and adsorptive/reactive adsorptive properties directed us to look at carbons from another perspective; from the perspective of nanotechnology. The results obtained by us and briefly addressed here are new and many questions have arisen, and are left unanswered, and many approaches need improvements. One has to take into consideration that explaining the complex phenomena in nanoporous carbons is not easy owing to the combination of the porosity and surface chemistry effects. Practically either one cannot exist without another and they add up to that's specific and unique synergy provided only by these materials. One thing is certainly true: “adventurous” graphene features can be found in nanoporous carbons and they deserve to be explored and used to their full extent.

Keywords

nanoporous carbons, porosity, surface chemistry, adsorption

PL02

Nanoreactors as catalysts for electrochemical processes for green energy applications

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Abstract

Nanoreactors are structures of materials defined at the nano level scale with an internal cavity and the ability to encapsulate one or more molecules guests. Encapsulation can not only isolate the guest from the bulk, but also help to induce specific conformation of the guest(s). Furthermore, confined space within a nanoreactor increases the concentration of reactants and can effectively influence the reaction rate inside the nanoreactor through binding interactions. These features result in various applications for nanoreactors, especially in catalysis, specially, concerning to oxidation and reduction reactions needed in many energy systems like batteries or electrochemical cells such as those used for CO₂ or nitrates reductions as new green alternative processes to the currently considered as standards based on fossil feed stocks. Correct choice of ligands and /or catalyst metal ions, are essential conditions for assembly of these nanoreactors. Two kinds of ligands (one-dimensional and two-dimensional ligands) can be used for assembly in the nanoreactors. One-dimensional ligands which form the edges of the coordination cage can bridge only two metal centers, while the faces of the final structure are formed by two-dimensional ligands which are like bridge between parts with different functional catalyst appropriate for the different steps of the overall catalytic process. It is known that the higher wall-to-volume ratio in nanoreactors with respect to conventional routes allows to effectively quenching radical-type reactions and runaway effects. In nanoreactors, the further increase of one-two order of magnitude in the wall-to-volume ratio will further increase safety of operations.

In this contribution we will be focused on examples for sustainable chemistry and more eco-efficient chemical syntheses routes. The reported nanoreactor examples facilitate safer and more energy-efficient production routes, higher-yield, cleaner and more resource-efficient synthesis of large volumes of chemicals: reduction of CO₂, reduction of nitrate and application in Lithium Sulphur, LS, battery will be assessed and discussed, showing with these examples the advantages in the use of this approach demonstrating that the integration between nanoreactor and catalysis is thus a key factor towards scientific and technological breakthrough in electrochemical or synthesis processes for a sustainable energy systems.

PL03

Surface and Interface Engineering for High Performance PEMFC Catalysts

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Abstract

The proton-exchange membrane fuel cells (PEMFCs) are of increasing interest as a zero-emission mobile power source for electric vehicles. A critical technological roadblock to widespread adoption of PEMFCs is the development of highly active and durable platinum (Pt)-based catalysts that are indispensable for accelerating the sluggish cathode oxygen reduction reaction (ORR). This presentation will cover our research on understanding fine structure and composition differences among nanoscale Pt-alloy catalysts and the effect of such nuanced differences on their catalytic performance in ORR. Combining theoretical modelling and experimental observations, we further developed a binary experimental descriptor that can be used to comprehensively predict the activity and stability of Pt-alloy ORR catalysts. In addition, we show that by creating a near surface environment that facilitates the shuttling of reactants and products, the catalytic activity can be effectively improved, leading to high PEMFC performance.

PL04

Organic Semiconductor Photocatalysts for Water split, Pollutant Degradation and Tumor Removal under Solar Irradiation

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Abstract

Organic supramolecular photocatalysts with full visible spectrum response has been successfully developed. The texture structure, crystal structure, photoelectric physicochemical properties, organic electron energy band structure, photocatalytic oxidation and anticancer properties can be adjusted via molecular structure and stacking structure. The photocatalytic activity came from molecular dipole, ordered stacking and nanostructure.

Self-assembled PDINH supramolecular is an effective visible-light photocatalyst for the photodegradation of pollutants and for oxygen evolution. Strong π - π stacking between PDINH molecules enables effective long-range electrons delocalization and accordingly promotes photo-generated charge migration and separation, leading to its remarkable photocatalytic activity. The highly crystalline perylene imide supramolecular (PDI-NH) photocatalyst is prepared by a high temperature imidazole solvent method. The catalyst possesses a breakthrough photocatalytic oxygen performance ($40.6 \text{ mmol g}^{-1} \text{ h}^{-1}$), which is 1353 times than the ordinary supramolecular PDI.

The SA-TCPP can powerfully split water to hydrogen and oxygen at 40.8 and $36.1 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$ without co-catalyst. The degradation performances of SA-TCPP were over 10 times better than the inorganic photocatalysts. Supramolecular photocatalyst SA-TCCP of bio-safe amount, targeted injection into the solid tumor inside, completely kill the tumor within 10 min under the deep penetration of red light (600-700 nm) irradiation. The solid tumors was completely removed via photocatalysts injection and red-light irradiation.

A highly crystalline urea-perylene imide polymer photocatalyst has been successfully built, which achieves super efficient oxygen evolution production ($3223.9 \text{ } \mu\text{mol g}^{-1} \text{ h}^{-1}$) without cocatalysts. Its performance is 106.5 times higher than conventional PDI supramolecular photocatalyst. The g-C₃N₄/rGO/PDIP Z-scheme heterojunction has been successfully constructed and shows an efficient and stable photocatalytic overall water splitting performance with H₂ and O₂ production rate of 15.80 and 7.80 $\mu\text{mol h}^{-1}$, respectively, about 12.1 times higher than g-C₃N₄ NS. Meanwhile, the notable AQE of 4.94% (420 nm) and solar-to-hydrogen energy conversion efficiency of 0.30% are achieved.

Keywords

Photocatalysis, Organic Semiconductor

Keynote Session:

KN01

Hyphenated electrochemistry and optics: quantifying local degradation and inhibition processes with high space-temporal resolution

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Abstract

It is well accepted that so called electrochemical techniques allow studying corrosion, corrosion inhibition and coating degradation processes. Nevertheless, data interpretation can be very complex. For this reason electrochemical tests are usually accompanied by post-exposure analysis with spectroscopic and/or optic techniques amongst others. The general problem of this approach is that it does not give information about the initiation and growth of the processes of interest nor real time information crucial to interpret or complement the electrochemical data.

Over the last years our team has been working on the development of highly resolved image correlation techniques that can be hyphenated with electrochemical measurements (e.g. electrochemical impedance spectroscopy and electrochemical noise). Such an approach allows: (i) a clearer interpretation of electrochemical signals, and (ii) the acquisition of data almost right after exposure to electrolyte, thereby obtaining information normally lost in electrochemical tests. In this presentation the principle idea will be introduced together with a number of examples on how this approach can be used to: (i) visualize and quantify local protection at damaged coatings [1], (ii) corrosion inhibition [2] and (iii) local corrosion processes with a particular focus on the local degradation kinetics of intermetallics [3]. Image correlation under immersion unveiled amongst others, diffusion paths in coatings for inhibitor release and a rapid activation of intermetallics (< 60 s after immersion) showing different degradation kinetics depending on local intermetallic composition.

[1] P.J. Denissen, A.M. Homborg, S.J. Garcia, Surf. Coat. Tech. 403 (2022) 127966.

[2] A.M. Homborg, M. Olgiati, P.J. Denissen, S.J. Garcia, Electrochimica Acta, 403 (2022) 139619.

[3] M. Olgiati, P.J. Denissen, S.J. Garcia, Corros. Sci., 192 (2021) 109836.

Keywords

coatings, corrosion, inhibition, optics

KN02

Towards more sustainable hydrogen conversion by carbon nanotubes based hybrid electrocatalysts

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Abstract

Based on IEA forecasts, the need for energy storage capacity increases 50 times, up to 10 000 GWh, by 2040. This development together with decarbonization of industry lays foundation for the hydrogen economy where sustainably produced hydrogen serves as an energy carrier and industrial reagent. Electrochemical water splitting in low temperature electrolyzers is one of the most promising technologies for producing green hydrogen. In those devices, the water splitting proceeds via two half reactions, the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction met in the anode (OER). In acidic membrane electrolyzes, scarce platinum group metals (PGM) are utilized at both the electrodes to efficiently promote these reactions.

In acidic environment, the anode reaction is the major sources for energy losses but the cathode processes contribute to degradation and consequently, affect the durability and sustainability of the device. It is also well recognized that the known PGM reserves cannot cover the foreseen need for this application. Hence, developing durable HER electrodes, based either on earth-abundant elements or notable lower PGM loadings, is essential.

Carbon nanotubes (CNTs) can be used as a skeleton for fabricating various PGM free and low PGM hybrid electrocatalyst and electrodes for HER because CNTs have several beneficial properties needed for electrocatalysts: In addition to high conductivity and good durability, they have appropriate properties for fabricating 3D electrodes. One interesting electrocatalyst alternative is a high aspect ratio material comprising of Pt nanowires and particles on single-walled carbon nanotubes (SWNTs). These Pt/SWNT hybrid materials have good Pt mass normalized HER activity and durability shown in laboratory scale long term electrolyzer investigations. Those properties are attributed to favorable Pt clusters interaction with the SWNTs favoring formation of durable Pt⁰ structures. By modifications, electrocatalyst promoting efficiently hydrogen reactions under alkaline conditions can be also achieved.

Keywords

hydrogen evolution reaction, carbon nanotube, low Pt loading, electrolyzer

KN03

From supported 2D films to functionalization: modelling surfaces and interfaces with DFT calculations

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Abstract

Nowadays computing facilities allow to treat complex model structures of surfaces and interfaces relevant to many applications. In this talk, several examples of DFT modelling of metal/insulator interfaces are presented: single transition-metal atoms adsorbed on metal-supported oxide thin films, mixed-dimensional van der Waals heterostructures, and adsorption and self-assembly of organic molecules on low-index coinage metal surfaces. The computational results are critically assessed and compared to available experimental data, highlighting the role of theory in rationalizing and explaining relevant phenomena in surface science.

In details, a comparative DFT study of single (K, Au, and Pt) atoms adsorption over a wide range of metal-supported oxide ultrathin films (MgO on Ag and Mo, ZnO on Cu, Ag, and Au, SiO₂ on Pt and Ru, TiO₂ on Ag and Pt, ZrO₂ on Pt and ZrPt) is presented. The strength of the adsorption is shown to depend on a complex interplay between charge transfer phenomena, morphology and chemical nature of the oxide film.

Then, structural and electronic features of MoS₂ single-layer films growth on Au(111) are discussed, as arising from a realistic model structure accounting for the non-commensurate lattice coincidence at the base of the observed moiré pattern. Upon adsorption of pentacene, the formation of atomically thin pentacene/MoS₂ lateral heterostructures is observed on the Au substrate. Pentacene tends to self-assembly at the MoS₂ edges, leaving the inner regions of MoS₂ clean.

Next, the functionalization of Cu surfaces by means of N-heterocyclic carbenes (NHC) is examined. Understanding the influence of the substrate in the molecular arrangement is a fundamental step to employ these ligands in technological applications. Theory plays an important role in unravelling the key-factors driving the formation of islands, ribbons, or disordered aggregates.

Keywords

DFT calculations, 2D Materials, Van-der-Waals Heterostructures, Functionalization

KN04

Analysis of biomacromolecules at electrolyte/interfaces

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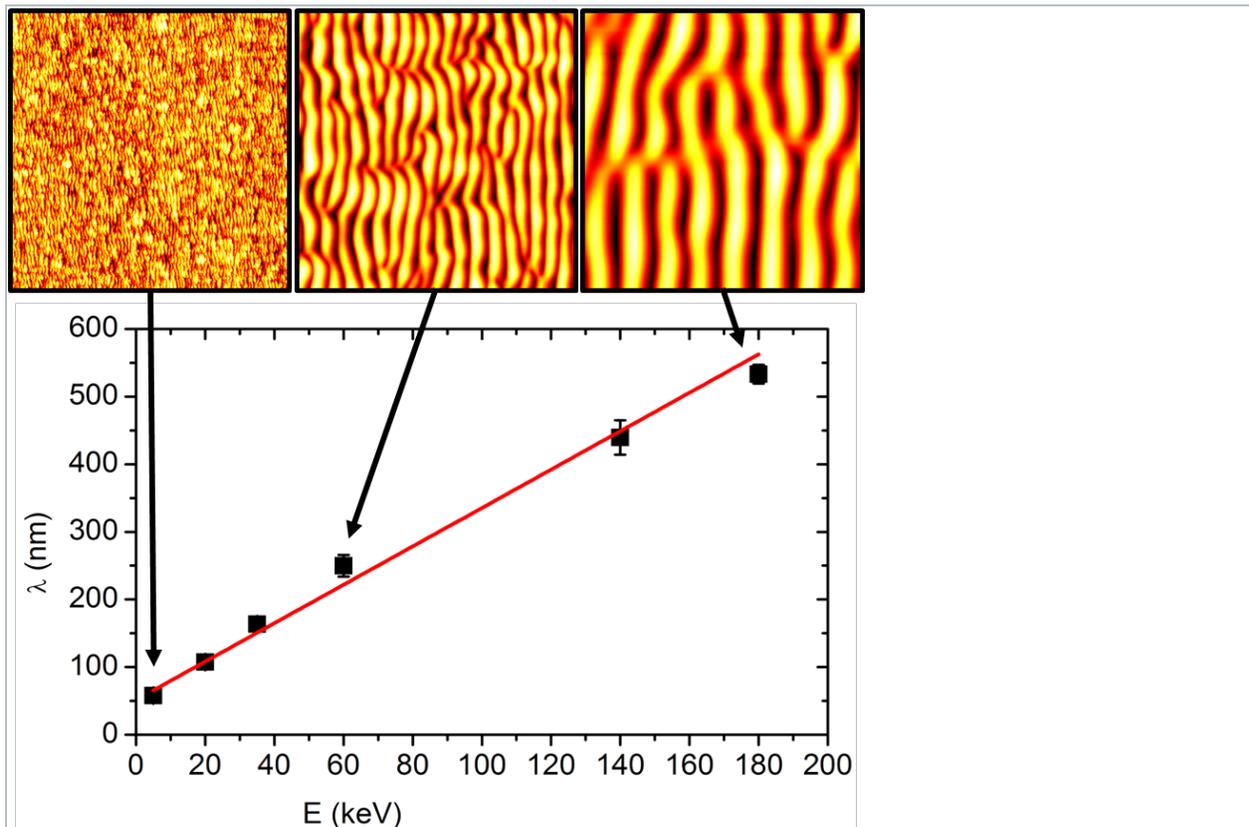
Abstract

Analysis of biomacromolecules at electrolyte/solid interfaces

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Technical and Macromolecular Chemistry, Paderborn University

Aspects of macromolecular adsorption and desorption processes at electrolyte/electrolyte interfaces play a major role in many systems. Fundamental analytical approaches in our research group consider e.g. amyloid adsorption and aggregation, protein adsorption on oxide covered bioresorbable alloys, and DNA origami based nanopatterning.



The presentation will mainly show how mechanistic and kinetic information of such interfacial molecular processes can be measured by the application of selected surface and interface sensitive methods. Moreover, the lecture will highlight the relevance of studying well defined model substrates such as self-assembled monolayers on gold, mica and bioresorbable iron based alloys with controlled microstructure.

Selected references:

1. A. Keller and G. Grundmeier, Amyloid aggregation at solid-liquid interfaces: Perspectives of studies using model surfaces, *Appl. Surf. Sci.*, 506 (2020) 144991
2. Protein Adsorption at Nanorough Titanium Oxide Surfaces: The Importance of Surface Statistical Parameters beyond Surface Roughness, Y. Yang, S. Knust, S. Schwiderek, Q. Qin, Q. Yun, G. Grundmeier, A. Keller, *Nanomaterials*, 11 (2021) 357.
3. Y. Xin, S. Martinez Rivadeneira, G. Grundmeier, M. Castro, A. Keller, *Nano Res.*, 13 (2020) 3142
4. Y. Yang, M. Yu, F. Böke, Q. Qin, R. Hübner, S. Knust, S. Schwiderek, G. Grundmeier, H. Fischer, A. Keller, Effect of nanoscale surface topography on the adsorption of globular proteins, *Applied Surface Science*, 535 (2021) 147671.
5. J. Huang, A. Gonzalez Orive, J.T. Krüger, K. -P. Hoyer, A. Keller, Guido Grundmeier, Influence of proteins on the corrosion of a conventional and selective laser beam melted FeMn alloy in physiological electrolytes, *Corrosion Science*, 200, 2022, 110186

Keywords

KN05

Dependence of morphology of titanate nanotubes on electrochemical etching synthesis temperature

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Abstract

By a simple electrochemical etching process, it is possible to anodize titanium substrate and grow ordered vertically aligned arrays of titanium oxide nanotubes. Titanium oxide is a well know and widely used semiconductor, whereas achieving titania in such nanostructured arrays significantly boosts the materials performance. Just by varying synthesis parameters like pH, reaction time, electrolyte, etc. the morphology and thereof functional properties can be easily modified and controlled to an extent.

In this work we examined the effect of reaction temperature during the anodization process, ranging from 4°C, 25°C to 60 °C. Samples were examined by grazing incidence X-ray diffraction (GIXRD), scanning electron (SEM) and atomic force (AFM) microscopy, diffuse reflectance spectroscopy (DRS), to define the critical structural, microstructural, optical and surface properties of derived and modified titania films.

The effect of the applied temperature was fairly obvious on the morphology of the samples. The appearance varied from fully ordered and well defined nanotubes to poorly grown tubular nanoporous surface. Also for the achieved nanotubes different circumferences and wall thicknesses were observed. Due to the high specific surfaces of the films, they were tested as immobilized photocatalysts for the degradation of waste pharmaceuticals. They have proven effective.

Acknowledgment: This work has been funded by the projects KK.01.2.1.02.0316 by ERDF, UIP-2019-04-2367 SLIPPERY SLOPE and PZS-2019-02-1555 PV-WALL by CSF.

Keywords

titanium oxide, nanotubes, electrochemical etching, immobilized photocatalysts

KN06

Hybrid Ceramic Coatings for Active Corrosion Protection of Light Alloys

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Abstract

The transport industry is currently seeking alternatives to substitute carcinogenic chromic-based treatments used up to now to improve the surface properties of light alloys. Plasma Electrolytic Oxidation (PEO) is an environmentally friendly electrolytic technique capable of producing ceramic coatings with improved hardness, adhesion, corrosion and wear resistance.

PEO coatings present a layered morphology formed by a nanometric and dense inner barrier layer and a thick outer layer with variable porosity. While the morphology of the inner layer cannot be modified, the porosity of the outer layer can be tailored as required during the coating synthesis. This porosity can serve as reservoirs for active species capable of providing smart functionalities to the coating. The active functionalisation of organic coatings has been studied in detail; however, the number of works focused on the functionalisation of ceramics is scarce.

The objective of this work is to achieve the active functionalisation of PEO coatings by incorporating corrosion inhibitors encapsulated into pH-sensitive nanocontainers. This multi-functionalisation allows the improvement of both corrosion and tribological properties simultaneously; the ceramic matrix will offer long-term wear protection, and the controlled release of encapsulated inhibitors will provide corrosion protection on-demand.

Two experimental approaches are presented, a single-step process, where the functionalisation is carried out while the coating is being synthesised and a two-step process based on a functionalisation post-treatment. The materials are characterised by FTIR, XRD and SEM and the corrosion properties are evaluated using electrochemical techniques (cyclic polarization and EIS). Special interest is given to the study of the self-healing properties of the coatings using localised electrochemical techniques (LEIS).

Keywords

Corrosion, Inhibitor, Plasma Electrolytic Oxidation, Light alloys

KN07

Emerging ultrafast laser technologies for elemental and isotopic materials analysis

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Abstract

In this talk we will provide a detailed overview of recent work on emerging femtosecond laser and non-linear optics approaches for detection of elements and isotopes. Technologies we will address include femtosecond filaments, ultrafast optical twisted photon beams and femtosecond-induced weakly ionized air plasma channels as sampling sources for long-range Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Molecular Isotopic Spectrometry (LAMIS) measurements. We will focus on LIBS and LAMIS spectroscopic signatures as well as femtosecond filament-matter interaction at distances >100 m. We will also discuss the effects of femtosecond laser filamentation on the formation of sub-diffraction limited self-organized structures on different targets, and turbulence effects on the pointing stability of gauss and twisted photon beams.

KN08

Correlating hydrophobicity to surface chemistry of microstructured aluminium surfaces and their use in Vibration Energy Harvesting (VEH) applications

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Abstract

Due to their superior physical and chemical properties, the use of aluminium alloys is widespread in applications ranging from automotive, aerospace, and naval industries to biomedical and household equipment. Aluminium alloys develop a natural oxide layer that is insufficient to avoid corrosion in humid and salty environments. For this reason, several methods to protect the aluminium alloy surface have been developed, including a change in the wettability properties (i.e. hydrophobicity or hydrophilicity). Though generally, approaches for super-hydrophobic modification of Al alloys surfaces imply two steps methods, in the last years, there has been an increasing interest in the development of one-step techniques avoiding the use of low surface energy substances which provide both economic and environmental advantages. Highly hydrophobic aluminium samples have been produced using a one-step facial method. It leads to a microstructured surface where etched regions characterized by rectangular building blocks coexist with flatter areas with much less pronounced corrosion effects. The microstructured Al samples have been investigated by Contact Angle Goniometry (CA), Scanning Electron Microscopy (SEM), and X-ray Photoelectron Spectroscopy (XPS) to correlate the surface wettability with the morphology at the sub-micrometer scale and with the chemical composition of the very first surface layers. The etched surfaces showed binary structures with nanoscale block-like convexities and hollows, which provide more space for air trapping. Both hierarchical micro/nanostructures and surface composition endow these surfaces with excellent hydrophobic properties. XPS analysis shows that the contact angle anti-correlates with the amount of metallic aluminium at the surface and confirms the essential role of the adsorption of airborne carbon compounds. The hydrophobic behaviour thus depends on surface morphology and surface chemistry combined. The most hydrophobic sample has been used for a feasibility test of a vibration energy harvester based on the Reverse Electrowetting on Dielectric (REWOD).

Keywords

Aluminium alloy, Hydrophobicity, Surface Chemistry, Vibration Energy Harvesting

KN09

Tailored microcaffolds for solar-light driven photocatalytic systems

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Abstract

Silica or multicomponent oxide (e.g. SiO₂-TiO₂ and SiO₂-TiO₂-HfO₂) microspheres with interconnected meso and macroporosity, also called MICROSCAFS, are attractive for many applications, including photocatalysis. Here, we show how they can be used as a platform for designing robust and efficient photocatalytic systems for a continuous flow reactor, allowing a low cost and straightforward purification of wastewater through solar-driven photocatalysis. MICROSCAFS are synthesized via sol-gel using a water-in-oil microemulsion and their interconnected macroporosity, consisting of sub-micrometer size pores, results from polymerization induced phase separation, by spinodal decomposition.

Insights about their step-by-step formation process will be presented, with the aid of Cryo-Scanning Electron Microscopy (cryo-SEM-EDS) applied to aliquots of the reaction batch taken at specific times during their synthesis.

Photocatalytically active microspheres were prepared by wet impregnation of the MICROSCAFS with Trizma[®] functionalized anatase TiO₂ nanoparticles (NPs), synthesized by a non-aqueous sol-gel method. NPs loading of ca. 22 wt% was obtained in the form of a thin and well-attached layer (Figure 1), covering the external surface of the MICROSCAFS as well as the internal surface of the pores. The TiO₂ loading leads to an increase of their specific surface area, without impacting the interconnected macroporosity, essential for an efficient flow of the pollutant solution during the photocatalysis tests. These were carried out in a liquid medium for the decomposition of methyl orange and paracetamol. Besides being photocatalytically active under continuous flow, they can be easily removed from the reaction medium, which is an appealing aspect for industrial applications.

Further optimization for the visible region of the solar spectrum is in place: recent advances on the MICROSCAFS' doping with gold NPs and rare-earth (RE) elements and the synthesis of RE-doped TiO₂ NPs, via a microwave-assisted solvothermal process will be presented.

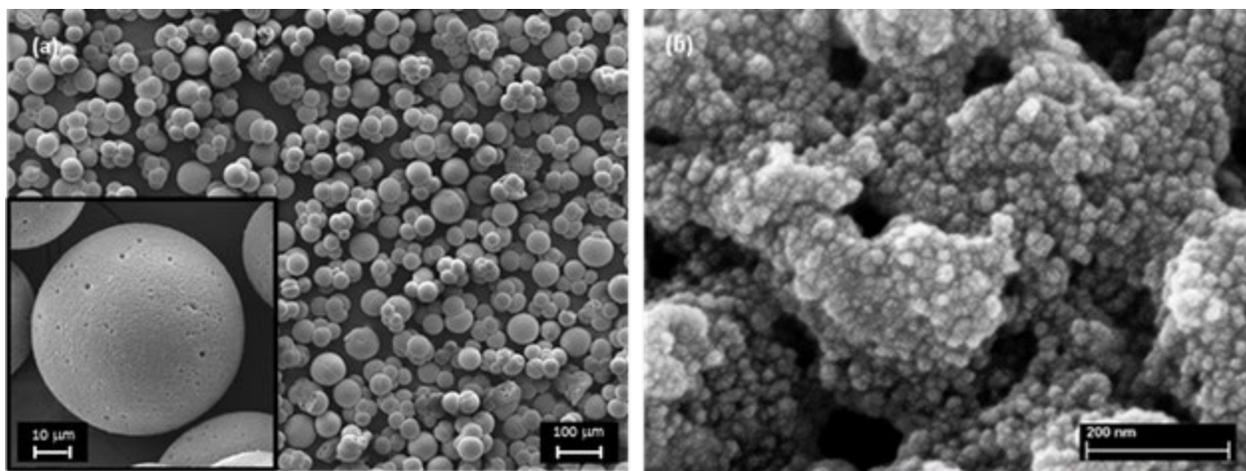


Figure 1. MICROSCAFS loaded with TiO_2 NPs at different levels of magnification

Keywords

porous microspheres, titania, photocatalysis, sol-gel

KN10

The role of artificial intelligence in minimizing analysis errors, illustrated with EXAFS and core level photoemission

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Abstract

We have developed artificial intelligence based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS) measurements. This development will help to address the reproducibility problems that slow research progress and inhibit effective tech transfer and manufacturing innovation in these scientific disciplines. A machine learning approach was applied to the analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy measurements collected using a synchrotron radiation facility. Specifically, a genetic algorithm was developed for fitting of the measured spectra to extract the relevant structural parameters. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. It requires the use of Larch and Feff for calculating the initial EXAFS paths. We have recently extended the code to make use of Feff8.5lite so it can calculate the paths needed for populating the analysis from within the EXAFS Neo package. Initial efforts have also begun to extend the code to the analysis of core level photoemission. The publication describing the analysis package and where to obtain the software can be downloaded at: <https://doi.org/10.1016/j.apsusc.2021.149059> or by contacting the speaker.

Keywords

Machine Learning, Analysis, EXAFS, XPS

KN11

Flow Through Atmospheric Pressure – Atomic Layer Deposition (AP-ALD) Reactor for Thin Film Deposition in Capillaries, and the Current State of X-ray Photoelectron Spectroscopy (XPS) Peak Fitting

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Abstract

We demonstrate the development of a new atmospheric pressure – atomic layer deposition (AP-ALD) system to coat the inner walls of capillary columns for gas chromatography (GC). Unlike traditional ALD, this reactor operates at near atmospheric pressure. Our new reactor addresses the challenges of depositing thin films inside capillaries, e.g., long pump down times, deposition in a very high aspect ratio material, temperature control, etc. We show ALD of alumina in 5 and 12 m capillaries (0.53 mm ID) via sequential half reactions of trimethylaluminum (TMA) and water. Our system yields pinhole free, uniform thin films. It includes small witness chambers for witness silicon shards before and after the capillary. A flow/transport analysis of the device is provided. Our ALD alumina thin films are characterized by spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX). Alumina film growth was 1.3-1.5 Å/cycle, which is consistent with previously reported results. For example, a thin, uniform (13-15 nm) alumina film was produced in a 12 m capillary from 100 TMA/water cycles, which took about 6 h. Film thickness measurements by SE on witness shards and by TEM at both ends of the capillary are in very good agreement. A capillary column coated with alumina was used to separate different gases by GC, although the retention times of the gases were essentially the same as with an untreated fused silica capillary. This successful deposition of ALD alumina opens the door for other possible ALD coatings, including hybrid organic-inorganic coatings, using the 450+ ALD precursors available. Time permitting, I will also discuss the state of X-ray photoelectron spectroscopy (XPS) peak fitting in the scientific literature, which is currently quite problematic.

KN12

Smart Zn: functionalization of Zn materials for biomedical applications

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Abstract

The current state-of-the-art shows that permanent implants are typically used in cardiovascular and bone healing applications. In transient processes, permanent implants often result in decreased life quality and an overload of healthcare systems for implants removal. Zn materials have a perfect behaviour that complies with wound-healing progression as they will degrade while tissue recovers over time.

Antibiotics are state-of-the-art approaches to overcome infections' increasing threat upon implantation. Concomitantly anti-inflammatory drugs are prescribed to decrease the undesirable host immune system responses and ensure adequate wound healing. The combination of different bioactive agents on Zn materials' surfaces can deliver smart solutions for transient applications and raise Zn smartness for such biomedical applications. To increase their smartness, the delivery of localized bioactive entities, through surface functionalization can be an answer to revert the clinical statistics of infections and inflammation as leading causes of implantation failure. Since Zn materials' functionalisation must result in a minimal impact on its degradation behaviour, the strategies used to raise its smartness will be discussed.

Keywords

Biomaterial, degradation, functionalization, surface; Zn and alloys

Oral Sessions:

O1.01

Multi-parameter discrimination between NSIP- and IPF-derived fibroblasts based on their physic-chemical properties

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Abstract

Idiopathic pulmonary fibrosis (IPF) and nonspecific interstitial pneumonia (NSIP) are two pulmonary disorders strongly mimicking each other. Although both diseases may have similar clinical presentations, including long-term cough and dyspnea, there are significant differences in their course and management. Moreover, in both cases the diagnosis is based on the exclusion of all alternative disorders, thus the diagnostic process is long, expensive and complicated and the new, reliable and fast diagnostic methods are highly required.

The aim of performed research was to find a set of parameters enabling discrimination between fibroblasts derived from IPF and NSIP. The viability of cells was recorded using MTS assay, their morphology and growth were traced using fluorescence microscopy, whereas mechanical properties of fibroblasts were studied using atomic force microscopy (AFM) working in force-spectroscopy (FS) mode. The experiments were performed for cells cultured on substrates with different elasticities modified additionally with ECM proteins, which should enhance any possible difference in examined parameters. Additionally, time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to determine chemical composition of fibroblasts. Obtained results depict that the discrimination between cell lines derived from IPF and NSIP diseased patients is possible based on the comparative analysis of cellular response to altered stiffness of the substrates.

This work was financially supported by the project National Science Centre agreement number UMO-2017/25/B/ST5/00575.

Keywords

idiopathic pulmonary fibrosis IPF, nonspecific interstitial pneumonia NSIP, substrate elasticity, force spectroscopy

O1.02

Adsorption of biologically-active molecules to polyurethane- quartz crystal microbalance study

Paulina Chytrosz-Wróbel, Joanna Słomka, Monika Gołda-Cępa, Andrzej Kotarba

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Abstract

The observations of the various length scales of cell arrangements in mammal tissues led to new approaches in designing biomaterials. Knowledge of fundamental mechanisms of cell-material surface interactions and a better understanding of interfacial processes at the cellular level consists a key factor for the development of tissue engineering. The nature of such interactions can significantly influence the fate of the implant. The attached cell behavior and function depend on the surface features of the polymeric substrate. It is therefore of the principal issue to design and tune surface properties to the most favorable for biomedical devices. In order to function properly in the human body biomaterials must also exhibit adjusted bulk properties, especially mechanical. One of the polymeric materials broadly used for the manufacturing of biodevices for specific applications are polyurethanes. The capacity of these polymers to undergo modifications increases their suitability for biomedical applications. RGD adsorption is proposed as the state-of-the-art approach for predicting the early-stage biological response of cells. This is often the first step before further experiments on complex peptides and proteins adsorption as well as cell adhesion, and thus consists of a milestone on the way to design a new generation of biomaterials. The goal of these studies is to determine the effect of surface oxygen plasma-modified polyurethanes on the adsorption of RGD peptide sequence and casein protein. The proposed research methodology includes both experimental (physico-chemical characterization by microscopic and spectroscopic methods) and theoretical (molecular dynamics simulations) approaches. The functional groups alter significantly the kinetics of peptide (RGD) and protein (casein) adsorption which is considered as biocompatibility predictor of the modified polyurethane surfaces.

Acknowledgment: This study was financed by the Polish National Science Centre project DEC2021/41/N/ST5/04128.

Keywords

Surface modification, biocompatibility, peptide adsorption, polyurethanes

O1.03

Growth interruption strategies for interface optimisation in GaAsSb/GaAsN type-II superlattices

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Abstract

GaAsSb/GaAsN superlattices (SLs), with type II bandgap alignment, have proven to be an optimal structure to be included as a 1.0-1.15 eV lattice-matched sub-cell in the design of high-efficiency monolithic multi-junction solar cells. However, preliminary growths of these SLs do not yet provide the desired photovoltaic efficiencies, as the structures are not fully optimized. For example, a strong segregation of Sb at the interfaces leads to severe deviations from the original design. To improve the quality of the interfaces, different growth approaches have been proposed in the literature, such as exposing the surface to different Sb fluxes before (soaking) and/or As fluxes after (desorption) the deposition of the GaAsSb layer. In this work, we analyze the effect on the interface quality of applying different interruption times at the soaking and desorption stages on the same GaAsSb/GaAsN SL grown by molecular beam epitaxy. The analysis of the structural quality and compositional distribution of Sb has been carried out by various imaging and spectroscopic techniques in a FEI Titan3 Cubed Themis double aberration-corrected scanning transmission electron microscope. The results show that the soaking and desorption process leads to significant improvement in the shape of the Sb content profiles. The profiles evolve from a more flattened shark-fin curve typical of the Sb segregation phenomena to a slenderer square shape as the soaking/desorption time is extended. The progressive increase in the slope of these profiles, leading to steeper interfaces, can be directly associated with the modifications of the segregation behavior during the soaking and desorption stages, which are discussed in the framework of the three-fluid-layer segregation model. Along with the improvement of the compositional sharpness, a simultaneous improvement of the roughness of the GaAsSb layers is also observed.

Keywords

GaAsSb/GaAsN Superlattices, Surface segregation, Growth interruptions, semiconductors

O1.04

The model of a porous medium to describe society

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Abstract

As society is one of the top products of science, it is essential to define it properly and explain the relations among its constituents, while the functional mechanisms must be rigorously established. Recently, the entire world has experienced a feverish condition induced by the accelerated spread of what is generically known as Covid-19, while major hidden problems of society were suddenly revealed. Here we show that a novel concept for society perceived as a porous medium is effective for substantiating its true nature and twigging its evolution. This physical model with a fractal-like structure crystallizes social hierarchies into an assembly of similar patterns, forming a unique and solid structure that accurately describes the essence of society. It enables a shift of paradigms within a diverse spectrum of sciences (social, political, medical, etc.), hence wielding significant matters. We found that specific terms like porosity (θ) and tortuosity (τ) characterize the activity of individuals inside social systems, and respectively stand for the difficulties these encounter. Our results demonstrate that a package of measures consisting of the pair $\{\theta; \tau\}$ belongs actually to a certain frame of political ideology; it equates the permissibility of the system, which is actually a direct measure for the impact created by a highly-important issue (e.g. medical: a respiratory virus outbreak). We forestall that this breakthrough will provide precise means for better understanding and efficient management of the current SARS-CoV-2 pandemic. For such situations, positive outcomes have been achieved in practice exclusively via a proficient oligarchic form of leadership.

Keywords

COVID-19, Dynamics of respiratory virus outbreak , Porous media , SARS-CoV-2

O1.05

Small peptides on solid surfaces: A molecular level description of the interface

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Abstract

The modification of inorganic solids with oligopeptides has fundamental and practical importance in many applications such as cell-material interaction, biosensing, biomineralization and molecular electronics. The control of the adsorbed layer at the molecular level is the main challenge in this concern. The adsorption of these molecules from aqueous solutions may, indeed, raise two main issues: (i) the omnipresence of adventitious contaminants, which considerably limits the selectivity of the characterization of the adlayer of interest, and (ii) the surface reactivity, and thus uncontrolled alteration of the inorganic solids in wet conditions (oxidation, hydration, dissolution, etc.).

Herein, we report the use of electrospray ionization for the deposition of a small peptide, L-Glutathione, under ultra-high vacuum on copper, a surface which exhibits a high reactivity in aqueous solutions. We show that ion beam deposition is a powerful way for the control of the adsorption process of small peptides, under conditions that preserve their molecular structure. This procedure, which may be extended to a variety of biomolecules, is particularly relevant when vacuum evaporation fails, due to the molecule disassembling during the sublimation process, or the molecular “landing” at the surface in the form of aggregates.

When the adsorption of peptides is performed in the liquid phase, we observe the unexpected build-up of a hybrid peptide-copper multilayers whose thickness may reach hundred nanometers. We show that the driving factors for this layer growth is (i) the generation of Cu^+ ions, due to the dissolution of copper surface in aqueous medium, and (ii) intermolecular interactions between peptide-copper entities mainly through a combination of electrostatic interaction and hydrogen bonds which stabilize the supramolecular edifice.

The experiments described here are carried out thanks to a combined set of surface characterizations in situ multi-technique UHV chambers, real-time monitoring in liquid phase and ex situ analyses.

Keywords

peptide, adsorption, XPS, ion beam

O1.06

Investigating and tuning biomineralization through enzymatic-controlled processes on surfaces

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Abstract

Surfaces are well-known to be a distinctive area where specific reactions can occur. In this work, we propose to highlight how, through the help of enzymes, the compartmentalization offered by surfaces can be used to study and control the space and time where the mineralization of calcium phosphate occurs. The mineralization of calcium phosphate is an intricate process deeply involved in the formation of bones. Although it has been studied over the last seven decades, this process remains still unclear, especially concerning the first steps.

In this study, in order to steer specifically the mineralization process onto the surface, the supersaturation of the medium was controlled through the *in-situ* generation of phosphate by an enzymatic reaction, calcium ions being already present in solution. This way, the immobilization of enzyme by layer-by-layer assembly (LbL) allowed to control the location where the supersaturation is generated and, hence, where the mineralization can start.

Indeed, we showed in this work that such control can be obtained and how it can be modulated through the tuning of the enzymatic activity. The study of these systems performed mainly on flat surfaces by AFM, QCM, XPS and SEM was completed by the incorporation of collagen proteins (known to be deeply involved in the formation and the structuring of bones) to the LbL and the study of its effects on the crystallization of the calcium phosphate.

Last but not least, these multilayers were also integrated in porous solids to yield micro reactors where mineralization could occur according to a nanostructured pattern and could benefit from the effect of the confinement.

Keywords

biomineralization, enzyme, layer-by-layer, QCM-D

O1.07

Functionalized nanomembranes for structural analysis of proteins by cryo electron microscopy

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Abstract

Here we present a method to create thin, biofunctionalized and selective membranes for structural investigations of proteins by cryo electron microscopy (cryo-EM). To create these membranes, a bottom-up approach was developed (**Figure 1**).

The membrane must be very thin to allow for high resolution transmission electron microscopy thus the polymer layer was created to be only a few nm thick. As polymer we used polyglycerol (PG) as it is hydrophilic and biorepulsive which therefore makes it ideal to prevent nonspecific protein adsorption.¹ The individual polymer brushes were crosslinked with each other, both to stabilize the polymer and to create a stable free-standing membrane later. For this we chose ethylene glycol diglycidyl ether (EGDGE) as it has two reactive epoxide groups to crosslink the freestanding alcohol groups of the PG and on top of that allows for a hydrophilic linkage. The PG-EGDGE surface was functionalized with a derivative of nitrilotriacetic acid (NTA) for selective attachment of His-tagged biomolecules *via* Ni²⁺ ions.

To transfer the membrane, polymethylmethacrylate (PMMA) was used in a multi-step process after which the PMMA layer was removed at last.

Subsequently, the NTA-functionalized membrane was treated with aqueous NiSO₄ solution to activate the NTA moieties. This permits to selectively bind proteins tagged with a histidine sequence to the membrane and to be analyzed by cryo-EM.

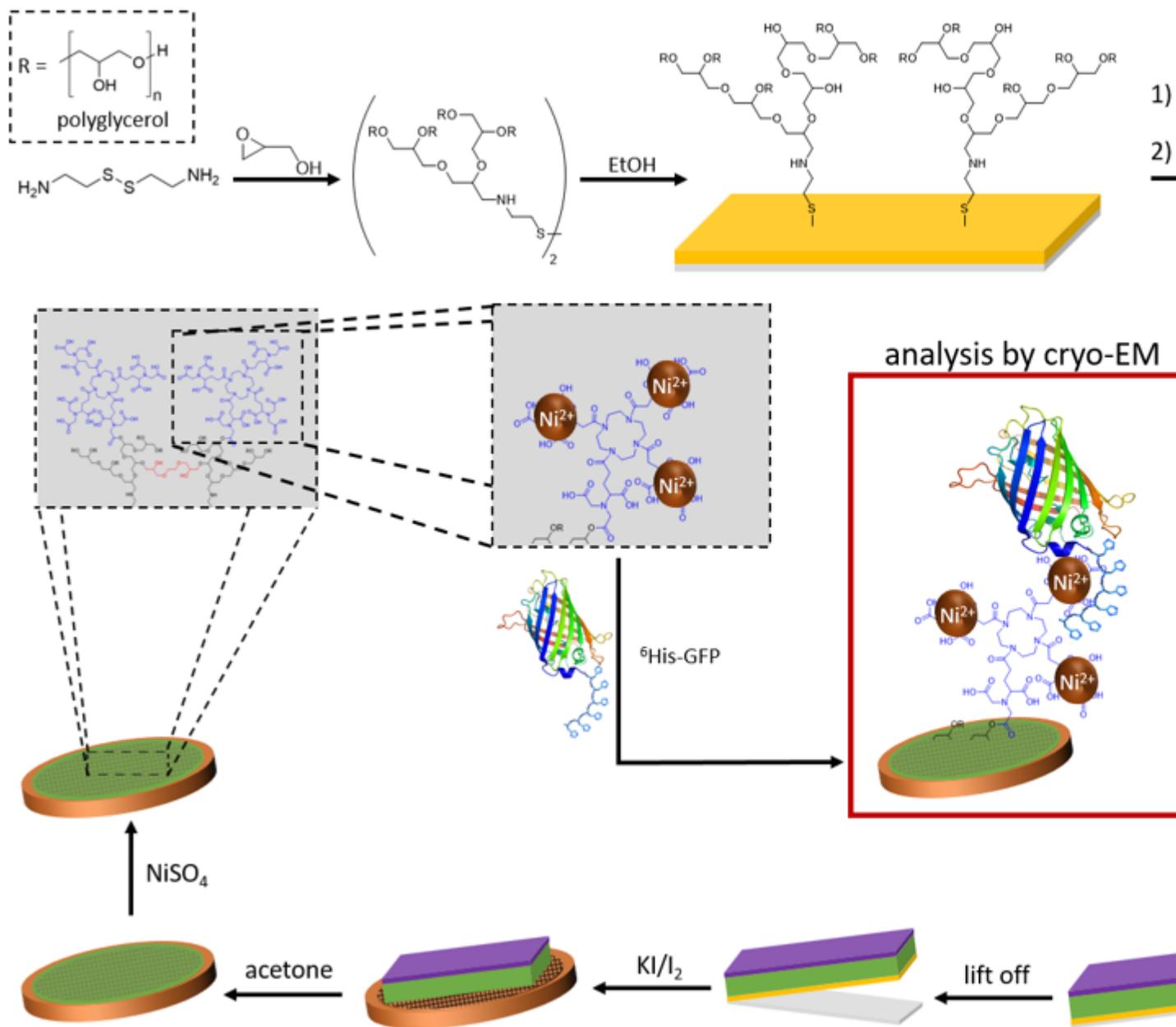


Figure 1: Bottom-up process for manufacturing NTA-functionalized membranes. A biorepulsive polymer layer is deposited via thiol groups onto a gold surface and stepwise crosslinked and functionalized. After a multi-step process, the free membrane can be loaded with Ni^{2+} ions and histidine-tagged proteins be selectively attached to be analyzed by cryo-EM.

[1] Scherr, J.; Parey K.; Klusch N.; Murphy B. J.; Balser S.; Neuhaus A.; Zickermann V.; Kühlbrandt W.; Terfort A.; Rhinow D., ACS Nano 11, 6467-647 (2017).

Keywords

biofunctionalized, membrane, cryo electron microscopy, biorepulsive polymer

O1.08

Immobilization of saponin on chitosan milliparticles as drug delivery system

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Abstract

With type II diabetes mellitus causing adverse health effects to over 3.6 million patients locally, there is a growing need to produce more diverse treatment options to cater for the general population. Conventionally, most drugs that regulate blood sugar level can cause hypoglycaemia and weight gain as side effects. As saponin had emerged to be a promising insulin stimulant with milder side effects, it is proposed in this research to coat on top of chitosan microparticles and milliparticles. The chitosan microparticles are produced via microfluidic technology using low-cost off-the-shelf setup and compared to previous work to verify the results. However, the main focus will be on the milli scale as it is easier to produce and upscale for mass production. When generated, milliparticles will form one of three shapes; “rugby” shaped, “red blood cell” shaped and “teardrop” shaped. A graph predicting the shape based on height and concentration of NaOH is generated with a proposed hypothesis for the observations. Milliparticles formed are approximately 1100 – 1500 microns in size. A comparison study was done for the treatment process in the methodology, verifying the necessity of using NaOH as solidifying agent, removing time-consuming intermediate drying steps and determining the necessity of immersing milliparticles in Phosphate Buffer Saline (PBS) solution. Successful immobilisation was verified by undergoing characterisation tests such as FESEM, EDX analysis and FTIR.

Keywords

Chitosan particles (CP), Milifluidics, Immobilization, Drug delivery system

O1.09

In situ coupled electrochemical-goniometry as a tool to reveal conformational changes of charged peptides

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Abstract

To control surfaces for manipulating cell functions is an interesting avenue for organic bio-electronics. Here we report on the electrical control of the conformation of charged peptides to be used in the electrical stimulation of cells. A stimuli-responsive self-assembled monolayer with specially designed charged peptides is used as a model system to analyze switching between two different hydrophilic states. The underwater contact angle is used to measure changes in the wetting property of an organic droplet under electrical stimuli. The observed variations in the UCA of the bio-interface may be explained by the difference in surface energy between the ON and OFF states. Molecular dynamics simulations in an electric field were used to test the concept that charged peptides alter orientation in response to electrical stimulation. Additionally, X-ray photoelectron spectroscopy (XPS) is used to confirm the electrodes' stability. Finally, we examine the prospect of employing this unique switching mechanism to describe bioactive surfaces. (1)

Reference:

1. Accepted article in Advanced Materials Interfaces (DOI: 10.1002/admi.202101480)

Keywords

Bioactive surfaces, Bioelectronics, Contact angle , Switchable Interfaces

O1.10

An electrochemical aptasensor based on nanoporous anodic aluminium oxide-gold nanoparticles-aptamer as a membrane-based biosensor for detection of SARS-Cov-2-RBD

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Abstract

Herein, we report an electrochemical membrane-based aptasensor for the determination of severe acute respiratory syndrome coronavirus-2 receptor-binding domain (SARS-Cov-2-RBD). For this purpose, first, the nanoporous anodic aluminium oxide membrane was fabricated electrochemically. Then, it was functionalized with 3-mercaptopropyl trimethoxysilane. Then, gold ion solution was passed through the membrane by a peristaltic pump. During this process, gold ions interact with the thiol group of 3-mercaptopropyl trimethoxysilane. After that, the immobilized gold ions were reduced to gold nanoparticles by sodium borohydride. The fabricated nanoporous anodic aluminium oxide-gold nanoparticles membrane was characterized by scanning electron microscope and energy-dispersive X-ray spectroscopy. After that, the nanoporous anodic aluminium oxide-gold nanoparticles were attached to the surface of the working electrode of a screen-printed electrode and then, a phosphate buffer solution (pH 7.4) containing thiolated aptamer was transferred into the cell by a peristaltic pump. After blocking the active site of the membrane with 3-mercapto-1-propanol, the aptasensor was washed with a phosphate buffer solution (pH 7.4). The fabricated nanoporous anodic aluminium oxide-gold nanoparticles-aptamer was characterized by the Fourier-transform infrared spectroscopy. The electrochemical behavior of the membrane-based aptasensor was examined using cyclic voltammetry and square wave voltammetry (SWV). The response of the proposed membrane-based aptasensor to the different concentrations of the SARS-Cov-2-RBD was investigated using SWV in the concentration range of 2.5-40.0 ng/mL. The limit of the detection was found to be 0.8 ng/mL. The analytical performance of the proposed membrane-based aptasensor was studied in a saliva sample.

Keywords

Electrochemistry, Aptasensor, Severe acute respiratory syndrome coronavirus-2 receptor-binding domain, Nanoporous anodic aluminium oxide membrane-gold nanoparticles

O1.11

Poly(amido amine) dendrimers adsorption kinetics on silica- hydrodynamic solvation effect.

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Abstract

Dendrimers represent an important group of macromolecules. Due to well-defined structure, presence of a large number of surface functional groups, pH-dependent charge they can be exploited as nano-carriers of drugs, antibodies and other active agents. However, the applications of dendrimers in biomedical sciences and medicine require a proper understanding of their solvation phenomenon leading to swelling or shrinking depending on the physicochemical conditions.

In our work, the total solvation was evaluated, comprising internal and external contributions of eighth generation poly(amido amine) dendrimers on silica (1). The porosity of the dendrimers, their internal solvation by the electrolyte and the dendrimer charges were determined by both the experimental methods (atomic force microscopy, quartz crystal microbalance, optical waveguide lightmode spectroscopy, streaming potential measurements, dynamic light scattering, electrophoresis) and theoretical calculations based on the hybrid random sequential adsorption approach. It was found that the total solvation comprises the internal and external contributions due to hydrodynamic coupling effect. It was confirmed that the hydrodynamically coupled electrolyte amount in dendrimer layers is many times larger than the internally coupled electrolyte responsible for swelling. It was also shown that the hydrodynamically coupled electrolyte mass depends on the sensor oscillation frequency (overtone number) and the dendrimer coverage. This indicates that in the interpretation of dendrimer swelling phenomenon one should consider the dominant role of the solvent coupling due to hydrodynamic effects.

1. Michna, A., Pomorska, A., Nattich-Rak, M., Wasilewska, M., Adamczyk, Z. J. Phys. Chem. C 2020, 124, 17684-17695

Acknowledgements

This work was funded by the National Science Centre, Poland, Opus Project, UMO-2018/31/B/ST8/03277.

Keywords

PAMAMG8, streaming potential of dendrimer monolayers, AFM , electrophoretic mobility of dendrimers

O1.12

Molecular dynamics simulation of surface-functionalized polyurethane

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Abstract

In biomedical applications, thanks to the unique combination of properties, one most commonly used polymer is aromatic polyether polyurethane. Owing to its amorphous structure, the material is elastic and has excellent hydrolytic stability. The bioperformance of this material can be improved by oxygen plasma functionalization. Such treatment increases biocompatibility, but at the same time significantly higher bacteria affinity to such surfaces is observed. The bacteria attach to abiotic surfaces, through adhesins (surface recognition molecules), investigations into these proteins' adsorption provide a good model to understand the role of biomaterial surface chemistry and bacterial affinity. Therefore, in the study, *in silico* molecular dynamics simulations were performed to provide the basis for a better understanding of the complex interplay between biomaterial surface properties and early steps of biomaterials-centered infection.

Molecular dynamics has been used to study the biomaterials interfaces, however so far for polymeric materials, most of the reports present models of crystalline polymers (e.g. PE, PTFE, PET). In the study, atomistic molecular dynamics simulations were used to create the amorphous polyurethane model. Such a model was then used to analyze the surface processes taking place on unmodified and oxygen-plasma modified polymeric materials. The calculations were performed using GROMACS software, simulated systems include 12x12 nm² surface models with the following oxygen-containing groups: -OH, -CHO, COOH, hydrated with 20000 water molecules. The model was built based on experimental results of XPS and SIMS, which confirmed that -OH functional groups dominate at the functionalized surface and are mostly attached to the aromatic ring of methylenediphenyldiisocyanate (MDI) fragments. In the broader context, the results of the performed MD simulations are unprecedented and will be used for the development of architecture of knowledge for fine-tuning the polymeric biomaterials surface properties.

This study was financed by the Polish National Science Centre project awarded by decision number 2019/35/D/ST5/03107

Keywords

polyurethane, biomaterials, molecular dynamics, surface functionalization

O1.13

Adsorption mechanism of carrageenan and stability of its layers on macroscopic surfaces

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Abstract

The aim of this research was to determine the kinetics of adsorption and desorption of carrageenan (negatively charged polysaccharide) on positive macroscopic surfaces.¹ These substrates were obtained by controlled adsorption of anchor layers composed of 8th generation polyamidoamine dendrimers (PAMAMD) and branched polyethyleneimine (bPEI) on silicon dioxide surface. The selected macroions are positively charged over a wide range of pH and ionic strengths, but differ in shape and polydispersity coefficient.

The bilayer system (carrageenan deposited on the anchor layer) was analyzed with the use of: streaming potential measurements (SPM), optical waveguide spectroscopy (OWLS), atomic force microscopy (AFM) and quartz microbalance (QCM-D). These research methods enable to determine the carrageenan adsorption mechanism, mainly controlled by electrostatic interactions. The obtained results show that the adsorption efficiency of carrageenan is correlated with: (I) the value of the zeta potential of the saturated anchor layer, (II) the type of transport (diffusion or convection) of the polysaccharide from the bulk to the solid/ solution interface and (III) the initial mass concentration of carrageenan aqueous solution. It was found that carrageenan adsorbs irreversibly and forms a stable layer on solid surfaces. Moreover, the bilayer system undergoes structural viscoelastic deformations along deposition of each biopolymer.

The obtained results, apart from their significance for basic sciences, can be used to develop procedures allowing to obtain biocompatible and stable macroion multilayers with well-defined electrokinetic properties for the use as biosensors.

This work was funded by the National Science Centre, Poland, Opus Project, UMO-2018/31/B/ST8/03277.

[1] A. Michna, J. Maciejewska-Prończuk, A. Pomorska, M. Wasilewska, T. Kilicer, J. Witt, Ö. Ozcan, J. Phys. Chem. B 2021, 125, 28, 7797–7808

Keywords

biofunctionalization, adsorption mechanism, macroion multilayers

O1.14

Novel surface engineering approaches for producing advanced synthetic heteronucleants promoting the crystallization of proteins of great biomedical interest.

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Abstract

Macromolecule crystallography is currently the most powerful technique for determining the three-dimensional structure of proteins at atomic resolution. However, despite its enormous level of technical development achieved, it is still limited by the great difficulty of obtaining crystals that, after exposure to X-rays, allow a high-resolution diffraction pattern from which the structure of the target protein can be elucidated. Hence, even today, the crystallization process is a trial-and-error procedure that requires enormous experimental effort and high economic costs. In this work, a novel surface engineering approach was adopted to produce a set of micro and submicro-scale patterns on polycarbonate (PC) flat surfaces that are used as a heteronucleating agents that promote, enhance or induce the nucleation and growth of protein crystals of three proteins of great biomedical interest: HsCNNM4₅₄₅₋₇₃₀, HsCBS_{Δ516-525} and MJ1004. Both, picosecond laser ablation (LA) and nanoimprint lithography (NIL) technologies were considered to produce the patterned surfaces, which were cut into tiny tablets (heteronucleants) by LA.

The results obtained from this study showed that though all patterns improved the percentage of nucleation, the crystal growth improved significantly upon increasing the Aspect Ratio of such regular patterns. The effect of laser cutting contributed to an increase in roughness and the random formation of micropores at the edges of the tablets. These two features together served as nucleation sites that favored a large number of new crystallization conditions. According to these results, the use of specifically designed microstructured polymeric surfaces with rough cutting edges increased significantly the crystallization conditions of proteins of biomedical interest than the ones obtained via controls and commercially available heteronucleants such as Naomi's Nucleant (NN) (Chayen, N. E. et al. PNAS. 2007; Saridakis, E. et al. Trends in Biotechnology. 2009).

Keywords

Polymeric heteronucleant, micro-scale pattern, picosecond laser ablation, protein crystallization

O1.15

Quantitative nanomechanical atomic force microscopy characterization of functionalized graphene in graphene field-effect biosensors

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Abstract

Since 2004, when it was isolated from graphite, graphene draw attention due to its peculiar mechanical, thermal, optical and electronic properties. Graphene field-effect transistors (GFETs) are a modification of the classic FETs in which silicon is replaced by a graphene layer. The one carbon atom thick layer guarantees improved charge carrier mobility and an enhanced sensitivity to electrostatic changes in its near environment. These characteristics make GFETs very interesting for biosensing. One of the posed challenges in the field is the development of protocols for graphene functionalization that are easy, cost-effective, and reproducible and lead to a homogeneous and broad coverage with a molecule which acts as probe for the target analyte. Moreover, for efficient detection, it is important that the analyte is found within the Debye-Huckel screening length, thus monitoring the thickness of the functionalized layer is fundamental. Atomic Force Microscopy was extensively used to characterize graphene topography, besides recent developments of the technique allow real-time monitoring of both topography and nanomechanical properties of the graphene. Nonetheless very rarely a thorough characterization of the GFETs in terms of surface chemistry is reported. In this work, we present an in-depth characterization of each step of graphene functionalization in terms of topography and nanomechanical properties to evaluate functionalization efficiency, homogeneity, graphene thickness. Moreover specificity for the target analyte was evaluated. We think that our approach provides valuable information to be exploited during the design GFETs biosensors.

Keywords

AFM, graphene, nanomechanical mapping, biosensor

O2.01

High-resolution imaging of active sites under reaction conditions for carbon-based electrocatalysis

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Abstract

Due to the abundance and the electrochemical versatility of carbon, it is becoming an increasingly popular material for electrocatalytic applications. Whether it is used as a support material, as a catalyst, or even as a bifunctional catalyst, insights into the reaction processes are of fundamental value. In this light, we employ electrochemical scanning tunneling microscopy (EC-STM) to in-situ evaluate electrode surfaces' behavior and identify the nature of the active sites. The experimental distinction between inactive and active sites of a catalytic system can be achieved by comparing the noise level of surface sites in the EC-STM signal while a reaction is 'Off' or 'On', respectively. The tunneling current will be stable under both conditions if the scanning tip is positioned over an inactive site. Over an active site, reactions occurring within the tunneling gap will influence the EC-STM signal, which can be observed as locally confined noise features superimposed on the surface morphology.

Here, we examine highly ordered pyrolytic graphite (HOPG) in alkaline and acidic media as a model system for carbon-based structures. In an alkaline medium, we compare the activity of specific surface sites under oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) conditions (**Figure 1a**).^[1] In both cases, predominantly steps and defects are active. However, in the case of the OER, the terraces also play a role. For the hydrogen evolution reaction (HER) in acidic media, it was possible to identify individual active sites on the 'honeycomb' structured surface with down to atomic resolution (**Figure 1b**).^[2] Apart from HOPG, the technique will be demonstrated for metal-organic frameworks, another class of promising catalysts for ORR and OER.

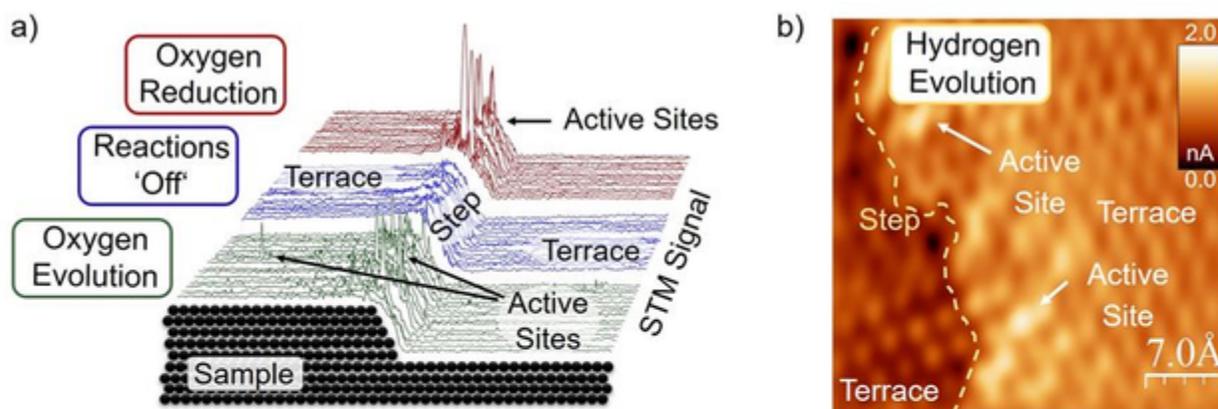


Figure 1: a) n-EC-STM measurement of a step under ORR (red) and OER (green) conditions, as well as during reaction 'Off' (blue). The most active sites in both cases can be found at steps, indicated by the distinct noise spikes at these positions compared to reaction 'Off'. Terraces are inactive towards the ORR. However, they do play a role in the OER.^[1] © 2021 Elsevier Ltd. b) Atomically resolved active sites on HOPG under HER conditions. Bright spots in the measurements indicate active centers. They can be observed predominantly at step edges and defects, while the basal plane (terrace) remains inactive.^[2] © 2021 The Royal Society of Chemistry

[1] Haid et al. *Electrochim. Acta* **2021**, 382, 138285.

[2] Kluge et al. *Phys. Chem. Chem. Phys* **2021**, 23, 10051.

Keywords

Scanning Tunneling Microscopy, Active Sites, Carbon Catalysts, High Resolution

O2.02

On the X-ray photoelectron spectroscopy analysis of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ material and electrodes

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Abstract

X-ray photoelectron spectroscopy (XPS) is a widely used technique to study surface chemistry and ageing mechanisms of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) based cathodes of lithium ion batteries. Analysis of the literature, however, reveals common problems in interpretation of their XPS spectra: 1) confusion of Ni2p spectra with Auger electron spectra (F_{KLL}) of fluorine from commonly used PVdF binder and from decomposition of the fluorinated electrolyte components, when the XPS spectra are acquired with Al $K\alpha$ X-ray source; 2) ambiguous fitting of the XPS spectral lines with several Lorentzian-Gaussian shapes leads to doubtful assignments of the oxidation states and questionable conclusions on the ageing mechanisms of the electrode materials. Revisiting the XPS data from aged NMC electrodes emphasizes the contribution of LiF and downplays the effect of nickel and manganese fluorides in the formation of cathode-electrolyte interface. To quantify $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio we introduce a novel method based on the ratio between Ni2p_{3/2} main peak intensity and intensity of the shake-up satellite. Applying this approach for commercial NMC333, NMC532, NMC622 and NMC811 powder materials we find good correlation with theoretically predicted values for freshly made materials.

Keywords

Li ion battery, NMC cathode, XPS

O2.03

Aerosol-assisted plasma processing for oil/water separation

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Abstract

For a long time, oily wastewater from domestic usage, petrochemical industries, and frequent oil spill accidents has posed a great threat to the environment and caused a series of environmental-related socio-economic problems. Efficient separation of oil/water mixtures has thus attracted more and more attention from both academia and industry. The membrane-based technique has recently been regarded as a promising avenue for oily wastewater remediation. However, the conventional wet-chemistry based membrane fabrication methods generally are expensive and involve a huge amount of toxic solvents, which may cause secondary pollution to the environment. Moreover, the fabrication efficiency and the required harsh reaction conditions for these conventional methods also significantly limit their further acceptance in the environmental application field. In contrast, eco-friendly plasma processing can be an alternative and promising surface modification approach for the fabrication of functional oil/water separation membranes. In this study, an aerosol-assisted plasma deposition method was proposed to functionalize polymer membranes with the aim to separate oil/water mixtures. 2-hydroxyethyl methacrylate was used as the polymerization monomer and injected into a plasma region in an aerosol form. The plasma was operated at very mild atmospheric pressure open-air conditions, and the fabrication process was very fast, in minutes level. As a result, a superhydrophilic and underwater superoleophobic thin film was successfully coated on an original hydrophobic polyester membrane surface. The surface morphology and surface chemistry of the plasma coating were investigated by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, atomic force microscopy, and scanning electron microscope. Moreover, the plasma functionalized membranes showed a superb separation efficiency towards various oil/water mixtures. This study thus contributes to a novel environmentally friendly method for surface engineering of oil/water separation membranes.

Keywords

aerosol-assisted plasma deposition, superhydrophilic membranes, underwater superoleophobic property, oil/water separation

O2.04

Novel 1D/0D metal sulfides - chemical conversion of CuS to Ag₂S at room temperature for electrochemical detection of glucose

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Abstract

Metal sulfides have attracted significant attention in the field of electrochemical sensors due to their exceptional electrical properties, such as high charge transfer coefficients and good conductivity. It was proved that they can exhibit improved glucose sensing ability compared to that of their oxides or pure metals. Moreover, it can be expected that the composite of different sulfides will exhibit synergistic activity of the components. To fully exploit this potential, the proper selection of the synthesis procedure is crucial. Especially important is the resulting morphology, which influences the electrochemical processes occurring at the surface and interface. Among the methods proposed in the literature, chemical conversion remains a facile and effective way to obtain composite metal sulfides.

This work aims to investigate the formation of CuS-CuS and CuS-Ag₂S interfaces and their influence on the electrochemical properties of materials. For this purpose, the room-temperature synthesis of 1D and 1D/0D copper sulfide structures was studied in detail. As precursors, copper sulfate and sodium thiosulfate were used, whereas as solvent served water and ethylene glycol mixtures in various ratios. Subsequently, CuS microtubes were sequentially converted to Ag₂S using a cation exchange method at room temperature. The progress of the synthesis and conversion was observed using an optical microscope and a scanning electron microscope (SEM) with simultaneous EDX analysis. Changes in phase composition were recorded by X-ray diffraction (XRD), infrared spectroscopy (FTIR), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The electrocatalytic performance of synthesized structures was evaluated based on electrochemical measurements of glucose level. Cyclic voltammetry (CV) was applied to determine the glucose oxidation peak. Based on chronoamperometric (CA) measurements, limits of detection and quantification, sensitivity, and linear range were assessed. The obtained results enabled us to profoundly study the interface in obtained microtubes and the way it translates into electrocatalytic behavior toward glucose oxidation.

Keywords

metal sulfides, chemical conversion, electrochemical sensors, glucose detection

O2.05

Anodic sulfate adsorption on vicinal Cu(111) electrode surfaces

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Abstract

Copper has been termed the “metal of the 21st century”. In particular, the electrochemical production of integrated copper circuitry (“Damascene Process”) has revolutionized information technology¹. The steadily decreasing dimensions of the wires and vias of the circuitry calls for a detailed understanding of the electrochemical behaviour of copper on the nanometer, even atomic, scale. This obviously turns the gaze on the influence of atomic scale surface defects in the underlying electrochemical deposition and etching processes. In this contribution we present in situ electrochemical scanning tunneling microscopy (EC-STM) results, i.e. registered in solution, on the reconstruction of well-defined vicinal Cu(111) electrodes of progressively reduced terrace width (e.g. Cu(21 21 16) and Cu(221)) in dilute sulfuric acid solution (H₂SO₄).

In contact with H₂SO₄ the flat reference Cu(111) electrode is known to reconstruct due to a strong interaction between copper and the sulfate anions, thereby forming a very stable Moiré – superstructure as shown in Fig. 1. A slight distortion of this superstructure leads to the formation of three 120° rotated domains, two of which are marked in Fig.1. Fig. 2 shows the distribution of terrace widths of the Cu(221) electrode after anodic adsorption of SO₄ – anions. All three widths (1.2nm (1); 2.1 nm (2) and 3,3 nm (3)) are significantly larger than the terrace width of the bare Cu(221) surface (0.74 nm), but fully consistent with multiples of the size of a Moiré unit (sketched in Fig. 1) in different orientation. The underlying adsorbate induced transport processes may be suited to control the surface topography of surfaces, e.g. before the deposition of further species, and confined systems.

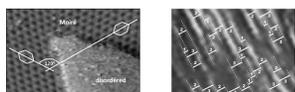


Fig.1 [(50 × 40) nm²] In situ EC-STM image of the sulfate induced Moiré superstructure on a Cu(111) electrode showing two of three possible rotational domains.



Fig. 2 [(20 × 10) nm²] In situ EC-STM image of the step pattern of a sulfate covered Cu(221) electrode surface. The only observed terrace width marked by 1, 2 and 3 are characteristically larger than that of the bare Cu(221) electrode (see text).

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Keywords

nano-electrochemistry, vicinal copper surfaces, sulfate adsorption, EC-STM

O2.06

In-depth study of correlation between titania surface properties and propyl-phosphonic acid modification

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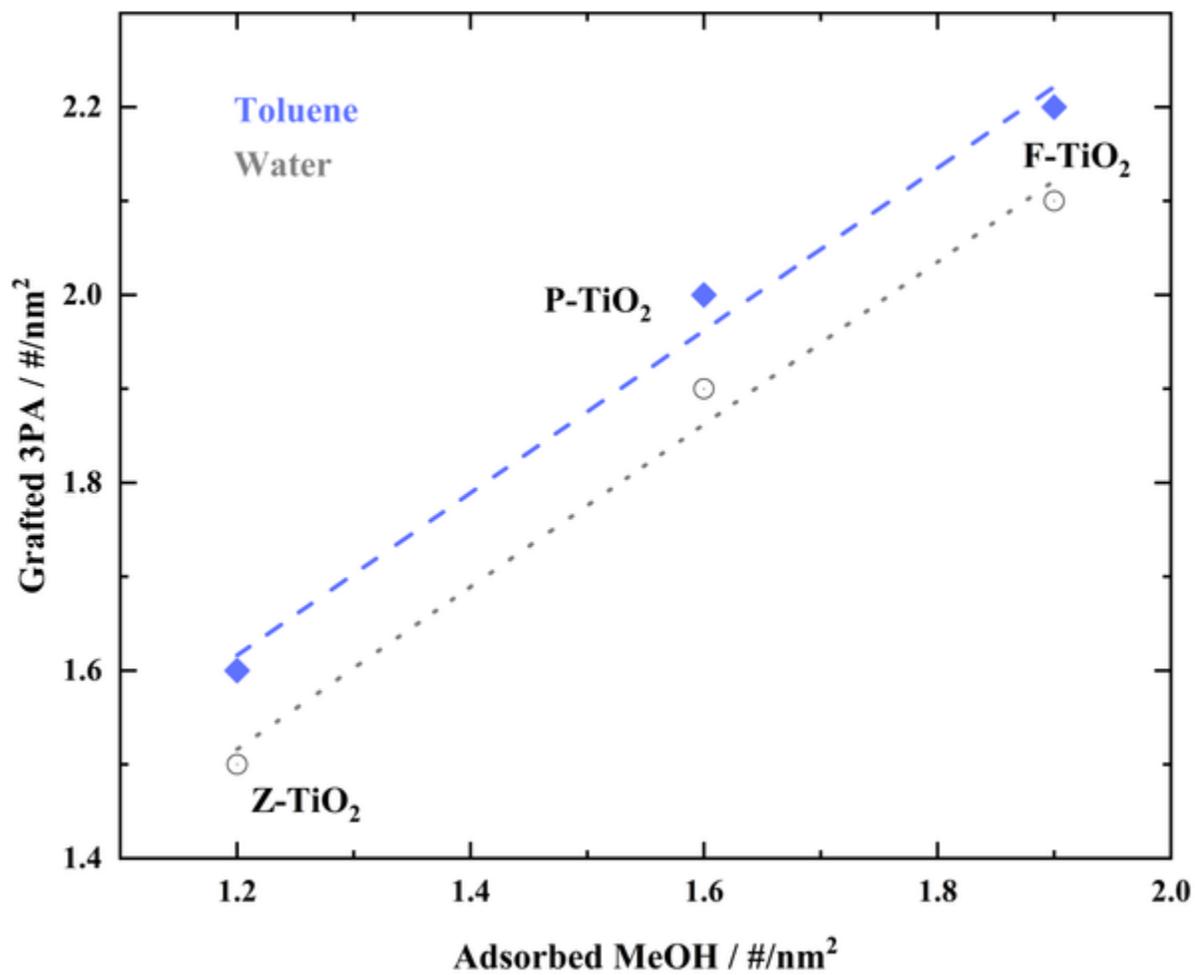
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Abstract

Organophosphonic acids (PAs) modification on metal oxides has been reported, but the correlation of titania surface properties and PAs modification is still lacking. This work studies three different titania supports (P-TiO₂, F-TiO₂ and Z-TiO₂) and compares their propyl-phosphonic acid (3PA) modification while keeping the reaction conditions the same. A clear difference in modification degree has been observed at the same concentrations of 3PA.

The in-situ DRIFT spectroscopy reveal that all the supports present different types of OH- groups and some hydroxyls on Z-TiO₂ and F-TiO₂ are difficult to be condensed even at 600 °C, while almost all OH- groups vanish on P-TiO₂ at 600 °C. The DRIFT spectra of supports modified with 3PA at the highest concentration in both water and toluene display that the consumption of OH- groups is closely related to the solvent used in case of F-TiO₂ and Z-TiO₂, but no big differences are observed on P-TiO₂.

Adsorption experiments between supports and solvents show that solvents affect the condensation of OH- groups on supports and these affected hydroxyls are the same as those which are left after 3PA modification on the supports and also with OH- groups that remain after heating at 600 °C. Further, MeOH sorption is applied to probe the OH- groups and Lewis acid sites on the different supports and elucidates that the surface activity is F-TiO₂ > P-TiO₂ > Z-TiO₂. Also here, a correlation is found between the OH- groups which cannot react with MeOH and those that are not able to be consumed by 3PA.



Keywords

supports, 3PA modification, hydroxyls, in-situ DRIFT

O2.07

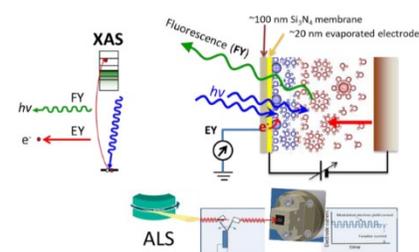
Interface Sensitivity in Electron/Ion Yield X-ray Absorption Spectroscopy: The TiO₂-H₂O Interface

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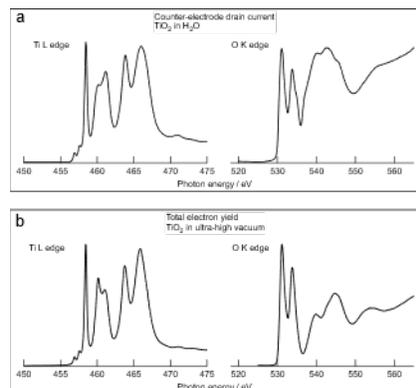
Abstract

Obtaining chemical information on solid-liquid interfaces is crucial to understand important processes, such as corrosion and electrochemistry. Unfortunately, very few techniques can give this information under *in situ* conditions.



Several years ago, soft X-ray absorption spectroscopy (XAS) was used to probe the Au-electrolyte interface¹. In these measurements, the X-ray absorption was measured via the sample drain current. Resembling the total-electron yield XAS of solid samples in vacuum, surface sensitivity was assumed. The sample of interest was deposited onto a SiN_x membrane thin (*ca.* 100 nm) enough to be X-ray transparent (Fig 1).

However, more recently a similar measurement mode was introduced, labelled as “total-ion yield”. It was claimed to be sensitive to the bulk of the liquid².



In this work³, the TiO₂-electrolyte interface is probed via both total-electron-yield and total-ion-yield configurations. The TiO₂ was deposited using atomic layer deposition, giving precise control over its thickness (6 nm). Both the total-electron and total-ion yield give essentially the same information, and both are interface sensitive (order of a few nanometers), contrasting previous claims that total-ion-yield measurements are bulk sensitive². This is clearly visible

after comparing the O K edge spectra of TiO₂ in H₂O (Fig 2a) with that of TiO₂ in vacuum (Fig 2b). In the former, the spectral features of oxidic O are dominated over those from H₂O. These findings are the first hard proof of surface sensitivity and convincingly show the potential of this technique to gain *in situ* understanding of fuel cells, batteries, and electrocatalysts. Furthermore, they show that the interfacial water on the anatase TiO₂ surface is bonded in an ice-like geometry.

References

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Keywords

TiO₂-water, NEXAFS, solid-liquid interface

O2.08

Unveiling the improved efficiency of ZnMg coatings against corrosion employing cluster models.

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Abstract

Despite Zn-rich ZnMg alloys being widely used as anticorrosive coatings, a sound understanding of their physico-chemical properties is far from being achieved yet. Indeed, this alloy has been shown to provide very good protective coating properties that even outperform those of pure zinc. However, the mechanisms that determine the corrosion process, triggered by fundamental structural and electronic properties, require a detailed quantum-mechanical analysis. To this end, we present a combined machine learning/*ab initio* exhaustive analysis of the corrosion process involving the formation and development of the oxide surface layer.

We employed nanoalloys as model systems to simulate the local environments and related complex processes that occur in extended granular surface coatings. The machine learning based Neural Network Potential model was used to simulate the corrosion process, and thereby providing with accurate data for subsequent Density Functional Theory calculations. The analysis involved the employment of structural descriptors, energetic descriptors such as the oxygen adsorption energies and excess adsorption energies, as well as electronic descriptors based on a topological analysis of the electron density and the electron localization function. We observed that small amounts of Mg create a very positive synergy between Zn and Mg which promote the growth of the oxide crust whilst protecting the core, which becomes the least reactive part within the system, being effectively disconnected from the surface in practical terms. Furthermore, Zn_2Mg and $Zn_{11}Mg_2$ compositions are found to be the best candidates to optimize the protection against corrosion in Zn-Mg alloys, in agreement with the experimental observations. Our results allow to better understand now why these compositions are better suited to the design of optimal protective ZnMg coatings.

Keywords

Corrosion coatings, Alloy, Oxidation, Neural Network Potentials

O2.09

Electrophoretic deposition of micro-quartz onto carbon fiber surfaces for an enhancement of bond behavior toward cementitious matrices

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Abstract

Micro-quartz (MQ) powder and micro-quartz/nano-silica hybrid (MQ/NS) are coated onto carbon fibers (CFs) using electrophoretic deposition (EPD) to enhance the interfacial bond performance between CF and cementitious matrix and improve slippage behavior at interface. The electrophoretic mobility of the MQ and MQ/NS particles with a negative charge in aqueous media in an electric field is confirmed by cyclic voltammetry (CV) and zeta potential tests. Quite a few MQ colloids and a large amount of MQ/NS particles are successfully coated onto fiber surfaces, as proved by scanning electron microscopy. Single-fiber tensile tests and thermogravimetric analysis (TGA) show that EPD treatment has only little impact on the tensile properties and thermal stability of modified fibers. However, storing the CFs in cement pore solution obviously impairs the temperature stability for untreated and modified fibers. Single-fiber pullout tests exhibit that the pullout behavior of MQ-modified CFs was dramatically increased due to the nucleating effect of quartz particles, whose pull-out mechanism is mainly controlled by friction. For MQ/NS-modified CFs, the coated NS could react with cement and generate hydrated products onto fiber surfaces, favoring the enhancement of interfacial bond behavior. Its bonding mechanism is of a more adhesive nature.

Keywords

carbon fiber, electrophoretic modification, micro-quartz, Cement-based composites

O2.10

Performance evaluation of adsorbent coated heat exchanger for adsorption desalination cycle

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Abstract

An adsorption desalination (AD) that exploits the physical and thermodynamic characteristics of the adsorbent and adsorbate is considered to be an environmentally friendly and yet low-cost desalination process. AD has received a great deal of attention because it produces two useful effects (i.e., high-grade fresh water and chilled water for cooling) using a low-temperature heat sources (< 85°C) found in industrial plants and a solar energy. However, AD has a limitation (i.e., low freshwater production) compared to other desalination process (e.g., MED, MSF, and RO). An enhancement of heat and mass transfer rate between the adsorbent and adsorbate is one of the crucial factors to improve the AD performance, and a promising method is to reduce the thermal resistance in the heat exchanger. However, a conventional granular adsorbent packed heat exchanger (GPHX) has the poor contact not only between the adsorbent and metal fins, but also among adsorbents, resulting in a low heat transfer efficiency. Hence, in this study, a powder adsorbent coated heat exchanger (PCHX) was proposed to improve heat and mass transfer rate. Here, main materials used to fabricate PCHX were an adsorbent (silica-gel), binders (styrene butadiene rubber and carboxymethyl cellulose), and a graphene. The thermophysical properties of the coated adsorbent was investigated based on adsorption isotherms of the argon and water vapor, and the thermal diffusivity and conductivity of the coated adsorbent were examined with the laser flash method. The performance AD cycle using PCHX was evaluated under specific operating conditions, and applicability of the PCHX was demonstrated by comparing the AD performance using the GPHX. Here, the AD performance was assessed in terms of specific daily water production (SDWP) and performance ratio (PR).

Keywords

Adsorption desalination, Silica gel, Graphene, Coating

O2.11

Decoupling of TaS₂ single layer from its Au(111) substrate by alkali intercalation

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Abstract

2D transition-metal dichalcogenides (TMDCs) have many potential applications in e.g. electronics, optoelectronics and spintronics. Bulk TaS₂ undergoes electronic instabilities, such as charge density waves and superconductivity, and their persistence at the 2D limit is an open question. Here, we focus on the growth of a TaS₂ single layer (SL) on a metallic substrate, Au(111), which induces electron doping of single layer (SL) TaS₂^[1] that varies spatially following the moiré. We demonstrate that this SL TMDC can be decoupled from its substrate by alkali (Cs and Li) intercalation, which lifts the moiré and relieves the associated inhomogeneous strain.

Scanning Tunneling Microscopy (STM, Fig. 1) shows triangular TaS₂ flakes on Au(111), and the herringbone structure reconstruction in between. A moiré is evidenced both by STM and reflection high-energy electron diffraction (RHEED). Grazing Incidence high-resolution X-Ray Diffraction (GIXRD) performed at the European Synchrotron (ESRF, BM32 beamline) provides more detailed structural information. In Fig.2, radial scans along the (100) direction show the evolution of TaS₂ and herringbone structures before, during and after the Cs intercalation. They evidence a highly oriented epitaxy of TaS₂ layer on Au(111) together with satellites that sign the moiré presence, due to a strong coupling between TaS₂ and Au. These satellites disappear upon intercalation, demonstrating a decoupling between TaS₂ and Au. Meanwhile, the herringbone structure becomes more intense and less ordered. The TaS₂ diffraction peaks evolution upon Cs intercalation shows that the TaS₂ lattice becomes more regular and is expanded. Asymmetric TaS₂ Bragg peak shapes indicate that a small (respectively a large) fraction is uncoupled before (respectively after) intercalation. Remarkably, the moiré pattern is recovered (the system re-couples) by annealing under H₂S, indicating the reversibility of the process.

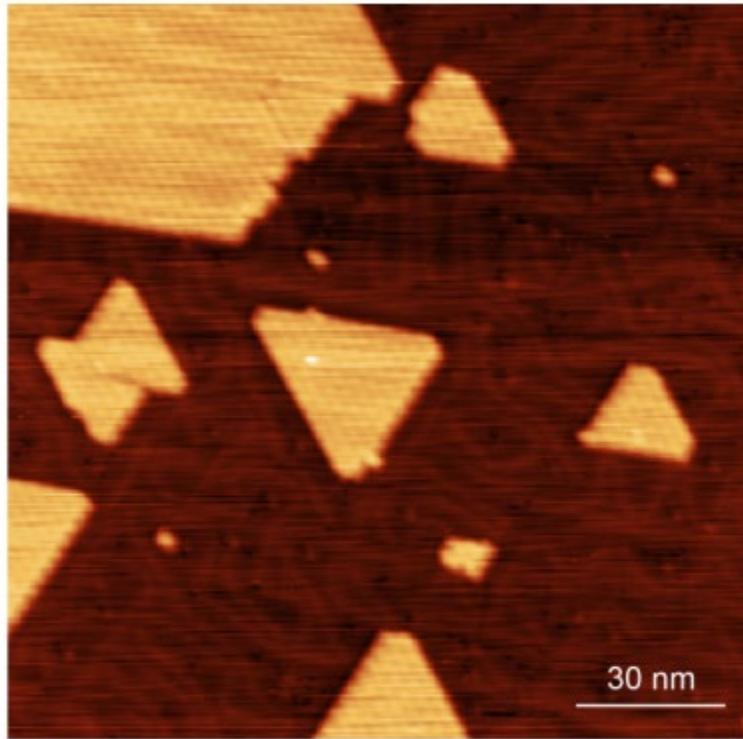


Fig.1: STM of TaS₂ grown on an Au(111) substrate. TaS₂ flakes are in yellow with the moiré appearing as darker hexagonally arranged dots. The substrate is dark, with the herringbone reconstruction appearing lighter.

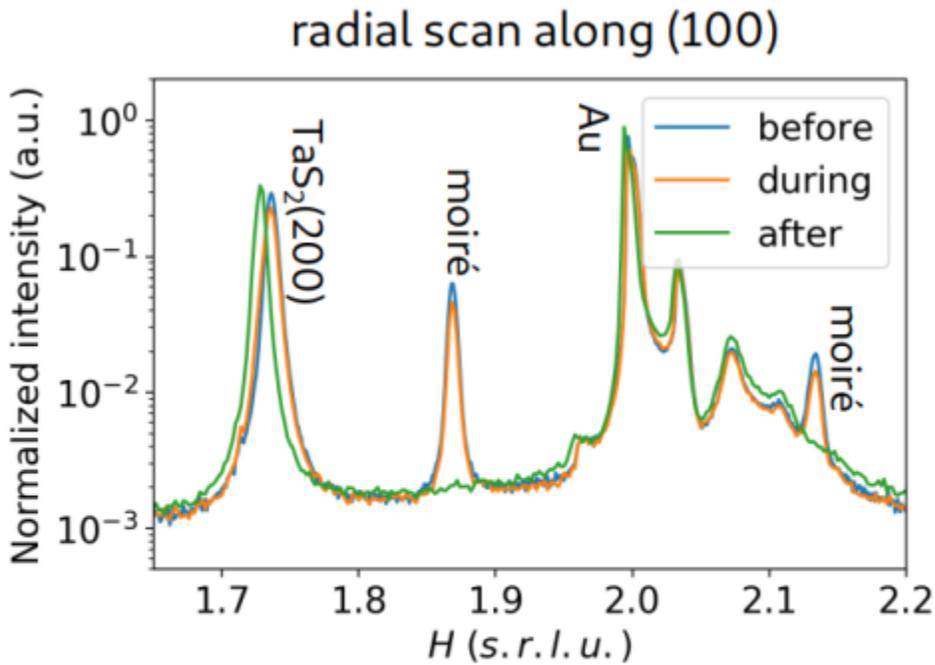


Fig.2: GIXRD radial scan measurements around the (200) Au peak, of a TaS₂ layer on Au(111) before (blue line), during (orange) and after (green) the Cs intercalation. The scattering intensities are plotted v.s. h in Au(111) surface reciprocal lattice units.

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Keywords

Transition-metal dichalcogenides, Epitaxy, Grazing Incidence high-resolution X-Ray Diffraction, 2D materials

O2.12

Exploring the formation of InAsBi/GaAs quantum dot structures by MBE.

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Abstract

The addition of small amounts of Bi during the growth of self-assembled InAs/GaAs(001) quantum dots (QDs) significantly influences their density and size, enabling longer emission wavelengths. Currently, the biggest technical challenge lies in the formation of InAsBi QDs by introducing sufficient Bi content inside the QDs. However, Bi has great problems to be incorporated into InAs as its solubility limit is only 0.025%, even lower than in GaAs, causing clustering, phase segregation or ordering phenomena. In this work, the possibility of formation of InAsBi/GaAs QDs samples with different Molecular Beam Epitaxy (MBE) growth conditions has been explored and evaluated by advanced Scanning Transmission Electron Microscopy (STEM) techniques. For this purpose, surface and buried layers of InAs QDs were grown at two growth temperatures (380 °C and 510 °C) under different Bi supply conditions (no Bi, low, medium and high fluxes).

On the one hand, at low temperature, QDs only form in presence of Bi. However, some QDs relax plastically accompanied by dislocations. On the other hand, regular QDs free of crystalline defects are observed in all samples grown at high temperature. At both temperatures, the QDs are larger as the Bi flux increases. In addition, nanometre-scale Bi compositional analyses have been performed to evaluate the presence of Bi within the QDs. At high temperature, Bi has not been detected in any of the QDs layers. In contrast, in the low-temperature samples, although Bi is clearly visible throughout the surface layer and especially in the surface QDs, it is also detected in some buried QDs, but in small amounts and not homogeneously. However, this opens the way for the future development of this type of nanostructures by refining the growth design.

Keywords

InAsBi quantum dots, STEM, EDX, Bismides

O2.13

Pharmaceuticals degradation over TiO₂-based photocatalyst exposed with different crystal facets

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Abstract

Recently, the surface structure's effect on photocatalytic activity has gathered an increasing interest among the scientific community due to its reported influence on the possible charge carriers trapping and separation. However, information about its effect on the degradation of various organic pollutants is generally missing. Therefore, our latest reports focused on studying the interactions between the exposed crystal facets of the anatase photocatalyst and its activity towards water purification from persistent organic compounds.

The obtained results have especially showed increased degradation rates and mineralization ability of the photocatalysts exposing {1 0 1} crystal planes when compared to the {1 0 0} and {0 0 1} ones. Moreover, the superior activity of the {1 0 1} nanostructures is observed despite their relatively low surface area. This fact could be connected with the high possibility of surface trapping of both electrons and holes on this crystal facet, which controls the number of reacting charge carriers. For the non-modified photocatalysts, exposing the majority of only one facet, the {1 0 1} have so far shown the highest activity towards degradation of persistent organic pollutants from the group of pharmaceuticals not susceptible to biodegradation.

Furthermore, new composites consisting of decahedral anatase particles exposing {001} and {101} facets coupled with accordion-like layered Ti₃C₂ with markedly improved photocatalytic activity were synthesized and studied towards carbamazepine, acetaminophen, and ibuprofen photocatalytic degradation. The obtained results indicated the promoting effect of Ti₃C₂T_x on TiO₂ activity under UV-Vis irradiation, which may act as a reservoir of photogenerated electrons, thus minimizing the recombination rate of electron-hole pairs. The hybrid photocatalysts showed remarkable efficiency in degrading all pharmaceuticals, with the removal efficiency in the range of 88-95% within 60 minutes under simulated solar light.

Acknowledgments

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Keywords

photocatalytic degradation, crystal facet engineering, pharmaceuticals photodegradation, titanium carbide

O2.14

Prominence of terahertz acoustic surface plasmon excitation in gas-surface interaction with metals

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Abstract

The current understanding of the dynamics of gas surface interaction is that all energy lost in the collision is transferred to vibrations of the target. Electronic excitations were shown to play a marginal role except for cases in which the impinging particles have energies of several eV. Here we show that this picture does not hold for metal surfaces supporting acoustic surface plasmons. Such loss, dressed with a vibronic structure, is shown to make up a prominent energy transfer route down to the terahertz region for Ne atoms scattering off Cu(111) and is expected to dominate for most metals. This mechanism determines, e.g., the drag force acting on telecommunication satellites which are typically gold plated to reduce overheating by sunshine. The electronic excitations can be unambiguously discerned from the vibrational ones under mild hyperthermal impact conditions.

Keywords

Acoustic Surface Plasmon, Cu(111), gas surface interaction

O2.15

Facilely synthesized nitrogen-doped reduced graphene oxide functionalized and/or co-doped with metal ions as electrocatalyst for oxygen reduction reaction

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Abstract

Due to the accelerated depletion of fossil fuels and accompanied environmental pollution, clean and sustainable energy technologies, such as fuel cells and metal-air batteries, have attracted extensive attention in both academia and industry.

To push further the research towards industrial application of these electrochemical devices, low-cost, durable and highly efficient electrocatalysts alternative to platinum are required to boost the oxygen reduction reaction (ORR). In this framework, noble metal-free metalloporphyrins supported on N-doped graphene have been proposed as innovative ORR catalysts characterized by notable stability and superior performance [1].

In the last years, a microwave-assisted method [2] has been optimized, to obtain heterogeneous catalyst for ORR starting from graphene oxide (GO), urea and a transition metal (e.g. Mn and Cu) precursor. We have proved that with manganese, our synthetic method originates porphyrin-like structures containing pyrrole rings within the reduced GO (rGO) basal plane, which coordinate the Mn²⁺ [2]. With copper [3], Cu²⁺ forms ionic tetra coordinated structures anchored at the rGO surface via residual oxygen containing functional groups. In both cases, the metal complex acts as a highly efficient catalytic reaction center for ORR and the identification of the catalytic center was strongly supported by several characterization techniques, such as X-ray Photoelectron Spectroscopy (XPS), Extended X-ray Absorption Fine Structure (EXAFS), X-ray absorption near edge structure (XANES) and Transmission Electron Microscopy (TEM) together with theoretical simulations performed by means of Density Functional Theory (DFT). All synthesized materials exhibit outstanding catalytic properties towards the ORR, as evidenced by electron transfer numbers larger than 3.8 and peroxide percentages lower than 7%, i.e. similar to those of reference Pt/C electrode.

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Keywords

reduced graphene oxide, oxygen reduction reaction, surface characterization, density functional theory calculations

O2.17

Probing the dynamic interfaces of SrTaO_xN_y with and without co-catalyst during visible-light sensitive water splitting

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Abstract

Oxynitrides (ABO_xN_y) are a class of semiconductors absorbing light in the visible range (380-700 nm). The size of the bandgap and the energy position of the band edges make oxynitrides promising candidates for visible-light-driven water splitting, with their performances enhanced by co-catalysts. Probing the physiochemical evolution of a thin film under operation conditions provides insights into the physical and chemical processes occurring in the material. The surface activity of the A and B-site cations in the presence of a co-catalyst at different voltage biases remains an open question.

With a custom-designed photoelectrochemical cell, operando shallow angle X-ray absorption spectroscopy (XAS) measurements are performed using thin films of the oxynitride semiconductor SrTaO_xN_y with and without co-catalyst during photocatalytic solar water splitting. Shallow angle XAS offers the possibility to investigate the structure and chemical state in the near-surface region of the films. Thin films possess relatively wide, well-defined, and atomically flat surfaces, representing ideal model systems for the investigation of the semiconductor surface. Using this approach, we are exploring the origin of the enhanced charge extraction with nickel-based (NiO_x) co-catalysts. NiO_x is among the most efficient noble metal-free co-catalysts for the oxygen evolution reaction (OER), suppressing the recombination of photo-generated electrons and holes.

The OER is the bottleneck of the overall water splitting process and an improved understanding of OER mechanisms for oxynitride thin films is required. Using the outlined approach, we aim at monitoring the physico-chemical evolution of the solid-liquid interface to answer open questions regarding the synergistic effects the co-catalyst has, and the role each cation plays. Addressing all these questions has large implications on the design and potential discovery of novel high performance materials.

Keywords

Semiconductor, Oxynitride, X-ray Absorption Spectroscopy, Photoelectrochemistry

O3.01

The influence of steric and ligand effects on metal- and alloy-supported oxygenated and hydrogenated Pt(111)

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Nottingham Trent University, Nottingham, UK

Abstract

Understanding the mechanisms of the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) is key to the development of modern energy storage and transport materials. The technology inherent in these materials contributes significantly to sustainable chemical production, whose energy footprint is an imperative concern when designing catalysts and networks of catalysts.

In this presentation a comparative study of the unreacted and reacted uniaxially strained Pt(111) and the layered (111)-Pt/Ni/Pt₃Ni and (111)-Pt/Ni/PtNi₃ surfaces has been performed using density functional theory (DFT) [1]. Through an analysis of the binding energies of oxygen and hydrogen over the high-symmetry binding positions of all surfaces, the study has shown that O and H tend to bind more strongly to the (111)-Pt/Ni/Pt₃Ni surface and less strongly to the (111)-Pt/Ni/PtNi₃ surface compared to binding on the equivalently strained Pt(111) surfaces. An estimate of the error in the computational binding energies as well as a critical comparative analysis of the binding mechanisms which contribute to these energetic differences has been performed by comparing the predictions of different density functionals. Changes in the surface magnetisation of the surfaces overlaying the ferromagnetic alloys during adsorption are highlighted and discussed, as well as the behaviour of the d-band centre across all surfaces to provide causal explanations of the mechanism changes.

[1] I. G. Shuttleworth, A Comparative Study of Oxygen and Hydrogen Adsorption on Strained and Alloy-Supported Pt(111) Monolayers. *Magnetochemistry* 2021, **7**, 101.

<https://doi.org/10.3390/magnetochemistry7070101>

Keywords

ORR, DFT, Strain, Pt

03.02

Machine learning for advanced optimization of carbon nanotube growth

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Abstract

Unique properties of single-walled carbon nanotubes (SWCNTs) make them prospective component of next generation electronics. A key barrier for this is a cost-effective and robust technology for the material with tunable characteristics. Despite all the advantages and advances already achieved in the field, industrial technology nanotubes with precisely tuned properties is still challenging. The lack of progress is usually attributed to the complexity of mechanisms for the nanotube nucleation, growth, and termination burdened by the lack of the general model, providing a quantitative relationship between the synthesis conditions and SWCNT parameters. Indeed, with the main features of the SWCNT growth are highlighted, the multiparametric nature of the chemical processes associated with the inconsistency of the results among reactors worldwide inhibits the precise control and demands a development of novel approaches to govern the process. In this work, we approach the problem with another vastly developing field which shows its best with multiparametric complex tasks – Machine Learning. We report the utilization of numerical models for processing of experimental dataset, obtained using a aerosol CVD reactor, based on the Boudouard reaction on the surface of Fe-based catalyst. We demonstrate the prediction of the reactor output (yield, diameter, and SWCNT quality) with an accuracy of as low as 4%, using temperature and reactants as input parameters [10.1016/j.carbon.2019.07.013]. For optimization of reactor operation, we also solve regression tasks and refine synthesis conditions to enhance the performance of SWCNT films as a transparent and conductive material. The strategy employed allowed us to fabricate films with sheet resistance at 90 % transmittance of $39 \Omega/\square$ — one of the lowest values achieved so far [10.1021/acs.jpcclett.9b02777]. Collected dataset accompanied by proof-of-the-concept experiments formed a basis for fine optimization of reactor performance. This work was supported by the Russian Science Foundation, grant 20-73-10256.

Keywords

carbon nanotube, aerosol CVD, catalysis

O3.03

Highly thermally stable multi-porous calcium aluminum hydrotalcite catalyst for efficient carbonate synthesis

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Abstract

In the context of a carbon-neutral era, conversion of greenhouse gas CO₂ via chemical catalysis is a powerful means. Using CO₂ and petroleum-derived alkylene oxide as the raw materials to produce high-value carbonate substances has been considered a green and economic path for carbon reduction and energy transition. We discovered a new multi-porous calcium aluminum hydrotalcite material (Ca-Al HTs), and found that it performs excellent catalytic ability on transesterification (an important reaction in the synthesis of carbonates). Being different from homogeneous basic catalysts such as soluble metal hydroxides and organic halide salts, and well-known solid basic catalyst CaO, which are difficult to recycle and suffer severe deactivation in long-term catalytic process, this new Ca-Al HTs catalyst with robust Ca₁₂Al₁₄O₃₃ crystal phase behaves much more stable catalytic performance, and did not have weight loss and structural damage during 4000 min efficient catalysis (63% conversion and 100% selectivity). The special crystal phase structure of Ca₁₂Al₁₄O₃₃ maintains stability at even a very high temperature of 900°C. In contrast, CaO as the reference catalyst is very sensitive to trace H₂O in catalytic system, and deactivates immediately (<20 min). The outstanding catalytic ability of Ca-Al HTs is attributed to its super-strong alkali strength, large alkali amount, and quick mass transfer originating from the hierarchical pore system.

Keywords

Thermal Stability, Hydrotalcite, Carbonate, Hierarchical pore

O3.04

Phase-dependent photocatalytic activity of bulk and exfoliated defect-controlled flakes of layered copper sulfides under simulated solar light

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Abstract

Sunlight-driven photocatalysis is an environmentally friendly approach to solve ecological issues. The development of simple yet sufficiently stable photocatalytic materials capable of responding to the full-spectrum light remains challenging. Here, we demonstrate the phase transformations of bulk copper sulfides from digenite (Cu_9S_5) to djurleite ($\text{Cu}_{1.97}\text{S}$) and low chalcocite (Cu_2S) by the reactive thermal annealing in ambient pressure chemical vapor deposition, followed by their top-down exfoliation. Using multiple techniques, we confirm that monoclinic Cu_2S is primarily formed at higher temperatures or greater reaction times and using reducing atmosphere. We measured the average thickness of approximately 4 nm of the exfoliated flakes with relatively large lateral sizes up to 10 μm . We tested the three phases of bulk copper sulfides and their exfoliated forms as photocatalysts for dye degradation under simulated solar light irradiation. Exfoliated Cu_2S flakes exhibited superior photocatalytic activity (0.007 min^{-1}), roughly twice higher than that of bulk chalcocite, which could be predominantly attributed to their 2D structure and also 2D planar defects, which could serve as active centers for dye photodegradation. Our study paves the way for developing next-generation full-spectrum-responsive 2D copper sulfide photocatalysts for environmental decontamination.

Keywords

Layered materials, phase transformations, 2D flakes, photocatalysis

O3.05

Reactivity of veratrol on Pt(111): adsorption and decomposition of a lignin β -O-4 linkage Model

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Abstract

To sustain the current attempts in valorizing lignin-based derivatives, the adsorption and decomposition of veratrol on a Pt(111) surface is studied as a model to understand the reactivity of the β -O-4 linkage in lignin. The results showed that under ultra-high vacuum conditions, hydrogen and carbon monoxide are the main desorbing products. Combining X-ray photoelectron spectroscopy, reflection absorption infrared spectroscopy and temperature programmed desorption experiments, a reaction mechanism is suggested, starting with the desorption of the multilayer around 215 K, followed by the decomposition of the monolayer through C-H and O-C bonds cleavage on the methoxy groups. 1,2-benzoquinone is proposed to exist as a key surface intermediate that keeps decomposing to form H₂ and CO that desorb at 315 K and 420 K respectively.

Keywords

veratrol, lignin catalysis, surface mechanism

03.06

Impact of the Schottky barrier height onto the photocatalytic activity of TiO₂+plasmonic metal solids under visible-light illumination

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Abstract

Visible-light triggered photocatalytic activity of the wide band-gap semiconductor TiO₂ can be improved by plasmonic properties of the noble metal Au. In the presented work, catalysts composed of different anatase TiO₂ supports (nanoparticles-TNP/nanorods-TNR) and 1 wt. % of Au were synthesized using wet-impregnation synthesis procedure. The size of formed Au ensembles in the catalysts was influenced by the difference in the zeta potential value of TiO₂ supports. The positive surface charge of TNR nanorods during the wet-impregnation synthesis and its higher specific surface area positively influenced the formation of Ti-O-Au(III) complex. The average Au cluster size in the TNR+Au sample (9.4 nm) was larger than in the TNP+Au solid (2.4 nm), where the surface of the TNP nanoparticles was negatively charged. The UV-Vis DR spectra of catalysts exhibited a broad absorption peak at 550 nm, which is typical for the plasmonic behaviour of Au clusters. A detailed XPS analysis of the valence band maxima (VBM, Fig. 1) showed that the value of Schottky barrier height (SBH) in the TNP+Au sample (0.31 eV) was almost double compared to the one in the TNR+Au solid (0.16 eV). The visible-light generated “hot electrons” in Au clusters of the TNP+Au catalyst need more energy and longer time to overcome the SB when injected into the TNP and have a higher potential to recombine with the generated holes in Au clusters. An additional advantage of the TNR support is its higher specific surface area, which means that the generated electrons can use a larger area to generate reactive oxygen species or oxidize adsorbed substrates. Higher photocatalytic activity of the TNR+Au catalyst was well expressed in the photocatalytic oxidation of water-dissolved bisphenols under visible-light illumination.

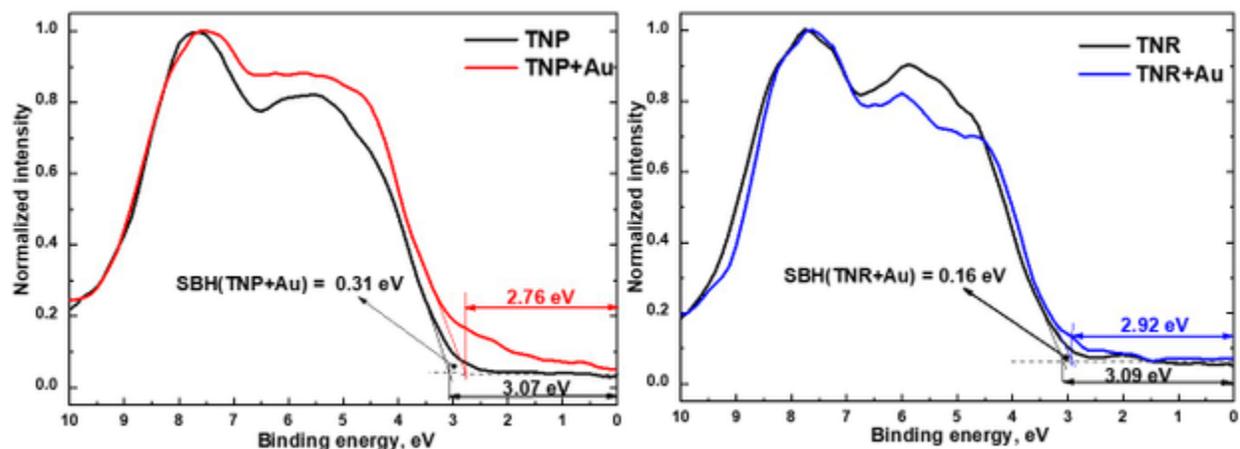


Figure 1: Determination of VBM of the investigated materials by means of XPS analysis.

Keywords

plasmonic photocatalysis, visible-light illumination, Schottky barrier height, TiO₂+Au catalysts

03.07

TiO₂/CuO bilayers for photoelectrochemical applications

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Abstract

Titanium dioxide is a flagship material in applications related to photoelectrochemistry, but there are serious limitations of its performance. Diverse strategies have been proposed regarding technology of stable and reusable materials with high photoelectrochemical efficiency. One of them is creating bilayered thin films, which is a heterostructure composed of two different semiconductors. This approach offers some advantages over a single layered material. The first advantage is widening of the range of light absorption. The second one is suppression of charge carriers recombination leading to their lifetimes increase. Additionally, in designing bilayers the surface structuring is also realized, which allows for a significant development of the specific surface area, important especially in gas sensing applications and photocatalysis.

In this work, in order to obtain *TiO₂/CuO* bilayers, cupric oxide was selected as a base component of the heterostructure, due to its chemical stability. Reactive magnetron sputtering was chosen as a method of thin film deposition. Firstly, different substrates were covered with cupric oxide and then a thin layer of the titanium dioxide of intentionally varied thickness was sputtered onto them without breaking a vacuum. As obtained bilayered materials were structurally characterized with the use of X-ray diffraction technique (XRD), X-ray reflection (XRR) and X-ray absorption spectroscopy technique (XAS). Morphology of thin films was studied by means of scanning electron microscopy (SEM). Transmittance and reflectance spectra of thin films over uv-vis-nir were analyzed in order to derive the band gap. Increasing thickness of TiO₂ overlayer manifest itself in XRR and reflection spectra above the absorption edge. Functional properties of the bilayers were examined by the photoelectrochemical methods.

Research financed by NCN Poland, decision no. UMO-2020/37/B/ST8/02539.

Keywords

TiO₂/CuO , bilayers, thin films photoelectrodes, magnetron sputtering

O3.08

Tuning of carbon nitride surfaces in light-driven, heterogeneous organocatalysis for C–C bond formation studied by low-field $^1\text{H}/^{19}\text{F}$ NMR relaxation measurements

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Abstract

Heterogeneous photocatalysis through metal-free catalysts has recently been attracting much attention for enabling organic synthesis by formation of C–C bonds. In this context, graphitic carbon nitride (*g*-CN) is an ideal semiconductor nanomaterial, which is already used in photocatalytic applications, such as hydrogen production. It is stable, it can be prepared by simple and scalable procedures, and surface properties and reactivity can be fine-tuned by introducing structural defects. While mainly used for photocatalytic oxidation reactions, there have recently been examples of C–C and C–heteroatom bond formation reactions, which are useful in organic synthesis.

In this work, post-synthetic modifications of the *g*-CN surface produced photocatalysts with fine-tuned surfaces that can effectively catalyze C–C bond formation. A robust correlation between surface properties and the catalytic behavior was established by the combination of detailed characterization, in particular, advanced low-field nuclear magnetic resonance (NMR) relaxation.

Keywords

Photocatalysis, Carbon nitride, NMR relaxation, Surface halogen bonding

03.09

Methanol decomposition on copper surfaces under ambient conditions: Mechanism, micro-kinetics and structure sensitivity

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Abstract

Methanol has the potential to become an important energy vector. The so-called "methanol economy" is essentially a carbon-neutral cycle consisting of two groups of reactions: Methanol synthesis from a mixture of CO, CO₂, and H₂, and methanol-to-hydrogen conversion reaction. Latter includes methanol decomposition (or dry dehydrogenation), partial oxidation, steam reforming, and autothermal reforming. Cu-based materials are currently our best option as catalysts, and they are already used industrially in some of the above-mentioned reactions. This makes the interface between Cu and methanol vapor exceedingly important. Yet, only a handful of experimental mechanistic studies, under realistic reaction conditions, are available in the literature. Herein, the interaction and decomposition of methanol on different copper surface orientations, Cu(111), Cu(100) and Cu(110), have been studied by means of PM-IRRAS and AP-XPS under 1 mbar methanol pressure in the temperature range of 25-100 °C. Our results reveal that methanol is dissociatively adsorbed on the clean Cu surfaces to form methoxy (CH₃O*) and hydrogen at ambient conditions. The temporal evolution of infrared spectra with time indicates that a transient state of high-coverage methoxy layer forms immediately after methanol exposure. For achieving an equilibrium coverage, the methoxy excess is eliminated via a further dehydrogenation to CO and its desorption to the gas phase. The kinetics of this process, which involves the activation of C-H bonds, displays a significant structure sensitivity with a much faster kinetics on the corrugated Cu(110) compared to the close-packed surfaces of Cu(111) and Cu(100). We also propose a model that explains the origin of the initial metastable methoxy coverage by considering the previous step of molecular adsorption in the form of H-bonded assemblies.

Keywords

Methanol dehydrogenation, Hydrogen production

O3.10

CO₂ hydrogenation to methanol over ZrO₂ supported Au catalysts: Activity, selectivity and mechanistic considerations

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Abstract

The global warming drives the scientific community to find strategies to reduce CO₂ emissions and the level of CO₂ in the atmosphere. The use of CO₂ as a feedstock has several challenges, therefore, it is necessary to discover new concepts and future opportunities for catalytic and industrial development. Among all the CO₂ conversion routes, most studies in recent years have been focused on CO₂ hydrogenation to methanol.

The use of nanometric gold nanoparticles supported on ZrO₂ enables efficient hydrogenation of CO₂ to methanol, even at low temperatures. Amorphous ZrO₂ supported 0.5-1 wt.% Au catalysts were synthesized by two preparation methods, deposition precipitation (DP) and impregnation (IMP). TEM analysis revealed that Au particle size distribution depends on the preparation method and Au loading, with the DP technique resulting in the formation of Au ensembles with 1 nm in size. TPD measurements revealed that the DP-based catalysts showed strong acidic sites and a high number of strong basic sites. Variations in surface sites due to different preparation methods exhibited a huge impact on the formation of intermediates and their hydrogenation to methanol. Important surface intermediates were identified by *in-situ* DRIFTS analysis, i.e. formate, dioxymethylene and methoxy species, which helped to establish a possible reaction mechanism via the formate route. Time-resolved FTIR profiles showed large differences in the hydrogenation of intermediates with respect to the catalyst preparation method. High CO₂ uptake and the presence of small Au nanoparticles enabled fast hydrogenation of intermediate species to methanol over DP-based catalysts, whereas low CO₂ uptake and the presence of bulk Au clusters leads to slow hydrogenation of intermediate species to products, as observed in the case of IMP-based catalyst. Au/ZrO₂ catalysts synthesized by the DP method enabled remarkably high rate of formation of methanol due to increased synergy between the metal and support.

Keywords

CO₂ hydrogenation, methanol synthesis, Au/ZrO₂ catalysts, *in-situ* DRIFTS

03.11

A novel and simple method for specific surface area optimization of g-C₃N₄ photocatalyst: Simplex

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Abstract

Heterogeneous photocatalysis has proven to be a new promising technology for wastewater remediation. In the usage of photocatalysts, new trends appeared by shifting to more environmentally friendly organic semiconductor, i.e. graphitic carbon nitride (g-C₃N₄) [1]. g-C₃N₄ is cheap, relatively thermally stable and active for degradation of water-dissolved organic pollutants under visible-light illumination. The drawback of g-C₃N₄ is its low specific surface area [1]. Therefore, the main objective of this research work was to synthesize g-C₃N₄ with high specific surface area and to use it for photocatalytic degradation of water-dissolved bisphenol A (BPA) under visible-light illumination. This was well achieved with the Simplex method, where a global maximum was found in just a few steps, which importantly decreased the required time and resources. Dicyandiamide was used as g-C₃N₄ precursor and four different base synthesis experiments were performed (denoted M1-4). By means of the Simplex method, we calculated new synthesis parameters for the M5 photocatalyst. M6 photocatalyst was synthesized as a comparison from literature [1]. As proposed by the Simplex method, the photocatalyst M5 exhibited the highest S_{BET} among the investigated solids (Table 1). Photocatalytic activity tests of the prepared solids towards the degradation of water-dissolved BPA under visible-light illumination were carried out in a batch slurry reactor operating in the kinetic regime. The obtained results illustrated in Figure 1 clearly demonstrate that in comparison to the M6 solid, the optimal M5 photocatalyst oxidized twice the amount of BPA after 120 min of reaction time.

Table 1. Specific surface area and synthesis conditions of investigated photocatalysts.

Sample	S_{BET}	End temperature	Temperature ramp	Time
	(m^2/g)	($^{\circ}\text{C}$)	($^{\circ}\text{C}/\text{h}$)	(h)
M1	29.4	550	150	4.00
M2	3.8	450	100	6.00
M3	9.9	550	600	2.00
M4	42.2	600	300	4.00
M5	74.4	683	600	0.67
M6	15.8	550	300	4.00

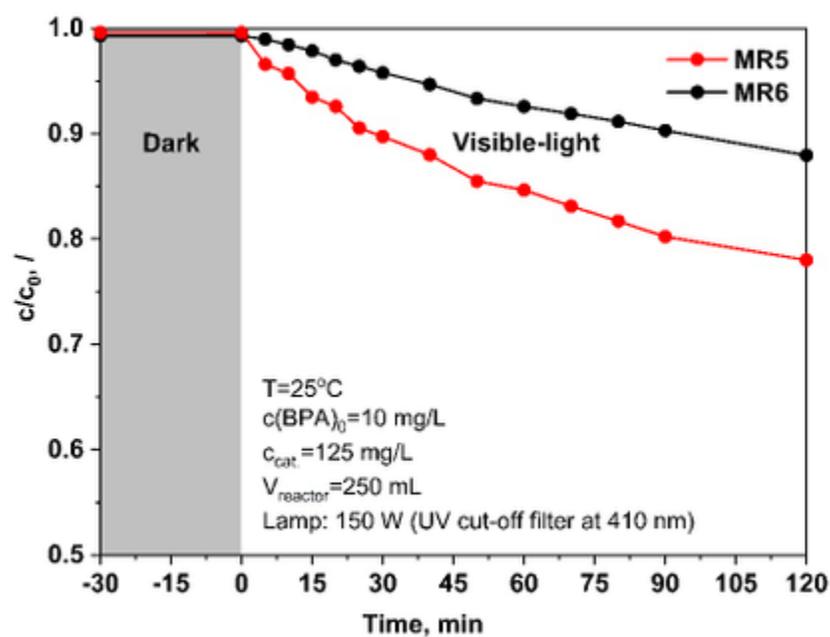


Figure 1. Photocatalytic degradation of water-dissolved BPA in the presence of M5 and M6 samples under visible-light illumination.

References

- [1] N.F.F. Moreira, M.J. Sampaio, A.R. Ribeiro, C.G. Silva, J.L. Faria, A.M.T. Silva, *Appl. Catal. B* 248 (2019) 184-192.

Keywords

g-C₃N₄, Simplex method, specific surface area, visible-light triggered photocatalysis

O3.12

Deposition of lithium on single crystal TiO₂(110) and nanoparticulate titanium dioxide with potential photocatalysis applications

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Abstract

Tuning the electronic properties of semiconductors by deposition of dopants, including metals, is important for various applications, such as catalysis/photocatalysis and plasmonic materials. In the present study, the interaction of vapor deposited lithium with single crystal TiO₂(110) and titania nanoparticles has been investigated using X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) and inverse photoelectron spectroscopy (IPES). In the case of ultrahigh vacuum sputter-cleaned TiO₂(110), XPS demonstrates that Li penetrates into the bulk, but the diffusion is self-limiting, and it covers the surface by 10 monolayers worth of deposited metal. By this coverage, the work function reaches that of clean lithium (ca. 2.4 eV). Lithium-induced Ti³⁺ gap states are present even at low coverage, as evidenced by XPS and UPS. IPES demonstrates that the unoccupied TiO₂(110) 3d states disappear as they are filled by electrons donated by lithium. Similar experiments have been performed on TiO₂ nanoparticles and their films, and preliminary photocatalysis results are presented.

Keywords

Titanium dioxide, Lithium, Photoelectron Spectroscopy, Metallization

03.13

Robust room-temperature NO_2 sensors from exfoliated 2d few-layered cvd-grown bulk tungsten di-selenide (2H-WSe_2)

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Abstract

We report a facile and robust room-temperature NO_2 sensor fabricated using bi- and a multi-layered 2H variant of tungsten di-selenide (2H-WSe_2) nanosheets, exhibiting high sensing characteristics. A simple liquid-assisted exfoliation of 2H-WSe_2 , prepared using ambient pressure chemical vapor deposition, allows smooth integration of these nanosheets on transducers. Three sensor batches are fabricated by modulating the total number of layers (L) obtained from the total number of droplets from a homogeneous 2H-WSe_2 dispersion, such as $\sim 2\text{L}$, $\sim 5\text{--}6\text{L}$, and $\sim 13\text{--}17\text{L}$, respectively. The gas-sensing attributes of 2H-WSe_2 nanosheets are investigated thoroughly. Room temperature (RT) experiments show that these devices are specifically tailored for NO_2 detection. 2L WSe_2 nanosheets deliver the best rapid response compared to $\sim 5\text{--}6\text{L}$ or $\sim 13\text{--}17\text{L}$. The response of 2L WSe_2 at RT is 250, 328, and 361% to 2, 4, and 6 ppm NO_2 , respectively. The sensor showed nearly the same response toward low NO_2 concentration even after 9 months of testing, confirming its remarkable long-term stability. A selectivity study, performed at three working temperatures (RT, 100, and 150 °C), shows high selectivity at 150 and 100 °C. Full selectivity toward NO_2 at RT confirms that 2H-WSe_2 nanosheet-based sensors are ideal candidates for NO_2 gas detection.

Keywords

2D materials, ambient pressure CVD, sensors, semiconductors

03.14

Dual-functional anisotropic nanostructures based on SnO₂/SnS₂ as photocatalytic materials for energy conversion and degradation of liquid pollutants

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Abstract

In recent years, photoelectrocatalysis has attracted considerable attention for applications in wastewater treatment and solar hydrogen production. As a technique that combines photocatalytic processes with electrolysis, it offers various advantages compared to traditional powder-based photocatalysis, such as reduced recombination of charge carriers due to applied external bias, easier separation of a photocatalyst from solution, and enhanced long-term stability. The overall efficiency of photoelectrocatalytic systems also strictly depends on the light absorption and surface redox reactions. Therefore, the design of photoelectrode structure plays a crucial role in achieving the highest possible performance.

Among various photocatalysts, SnS₂ is a non-toxic, visible-light active semiconductor with a conduction band edge enabling hydrogen generation. However, it is vulnerable to photocorrosion. SnO₂, in turn, is a photoelectrochemically stable wide-bandgap semiconductor with high electron mobility and high oxidation ability. In the SnO₂/SnS₂ hybrid system, SnO₂ supports the operation of SnS₂ and improves its photostability.

In the presented work, we designed photoanodes composed of anisotropic flower-like SnS₂, SnO₂, and SnO₂/SnS₂ nanostructures deposited on titanium, etched titanium and indium tin oxide (ITO) substrates. The aim of this study was not only to investigate the effect of the created SnO₂/SnS₂ heterojunction on the prepared photoelectrodes' performance, but also to demonstrate the crucial role of the applied substrate/photocatalyst interface. Photoelectrodes were obtained via chemical bath deposition method and characterized using scanning electron microscopy, X-ray diffraction, Raman and optical spectroscopy, and electrochemical impedance spectroscopy. The examination of dual-functional photoelectrocatalytic properties was performed by combining measurements in photoelectrochemical cells (PECs) for hydrogen generation and photodegradation of organic dyes. We obtained current-voltage characteristics of the prepared photoelectrodes in dark and under white light illumination. Moreover, we studied the kinetics of photocurrent change upon a short impulse of light. Finally, photoelectrocatalytic decomposition of indigo carmine was investigated.

Keywords

photoelectrochemistry, SnO₂/SnS₂, anisotropic nanostructures, surface functionalization

03.15

Permanent Charge-Containing Polymer Interfacial Layers for High Efficiency Polymer:Nonfullerene Solar Cells

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Abstract

Organic solar cells with polymer:nonfullerene bulk heterojunction (BHJ) layers have attracted keen attention and still been extensively studied because of their encouraging power conversion efficiency up to ca. 18%. Basically, polymer:nonfullerene solar cells can be processed by employing wet-coating techniques at room temperature. Here it is noted that considerable amount of small molecular nonfullerene acceptor (NFA) is included in the resulting BHJ films. Normal-type and inverted type device structures can be applied for the polymer:nonfullerene solar cells. Compared to normal-type structures, inverted-type polymer:nonfullerene solar cells benefit better stability in terms of top electrode degradation because relatively stable high work function metals (Ag) can be deposited on top of active layers etc. For bottom electrodes in the inverted-type devices, however, metal oxide buffer layers (mostly ZnO) have been introduced to match the energy barrier for electron collection from BHJ layers. Undesirably, most metal oxide buffer layers need high temperature annealing and/or require additional ultrathin interfacial layers. To minimize the number of layers and keep low temperature processes, it has been reported to simply coat ultrathin polymeric interfacial layers on the electron-collecting transparent electrodes of substrates (mostly, ITO). In this work, it is demonstrated that an ultrathin interfacial layer with permanent charges can further improve the performances of inverted-type polymer:nonfullerene solar cells. The reason on the improved performances will be discussed on the basis of various surface characterization results including ultraviolet photoelectron spectroscopy etc.

Keywords

organic solar cells, polymer:nonfullerene, permanent charges, work function

03.18

Atomic Layer Deposition of Au-TiO₂ inverse opals for the visible light photocatalysis of dyes degradation

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Abstract

The pollution of waste water due to organic dyes used in the textile and chemical industries is an important environmental issue. Inverse opals (IO) offer a great potential for increasing the efficiency of their degradation by semiconductor photocatalysts such as TiO₂ by the synergy of high specific surface and photonic crystal properties [1]. Doping TiO₂ with gold nanoparticles is another possible strategy to enhance its photocatalytic activity by increasing its optical absorption in the visible range [2].

This work reports the synthesis of Au-TiO₂ IO films by Atomic Layer Deposition and the study of their visible-light photocatalytic activity for the degradation of methylene blue in water solution compared to pure TiO₂ IO and flat Au-TiO₂ films. The use of preformed nanoparticles with a narrow size distribution allows to better control their plasmonic properties including light absorption in the visible range. The morphology of Au-TiO₂ IO films and the distribution of Au nanoparticles have been analyzed by scanning electron microscopy (Fig. 1) and nano-SIMS. Their composition and structure have been investigated by XPS and Raman spectroscopy.

The degradation kinetics of methylene blue was studied using Au-TiO₂ IO films as visible light photocatalysts. Flat Au-TiO₂ films were also used for comparison.

It has been shown that doping of TiO₂ with gold nanoparticles allows to obtain a faster degradation which reaches about 95 % in 7 hours instead of 90 % after 14 hours with flat films. These results highlight the potential of Au-TiO₂ inverse opal films synthesized by ALD for visible light photocatalytic applications.

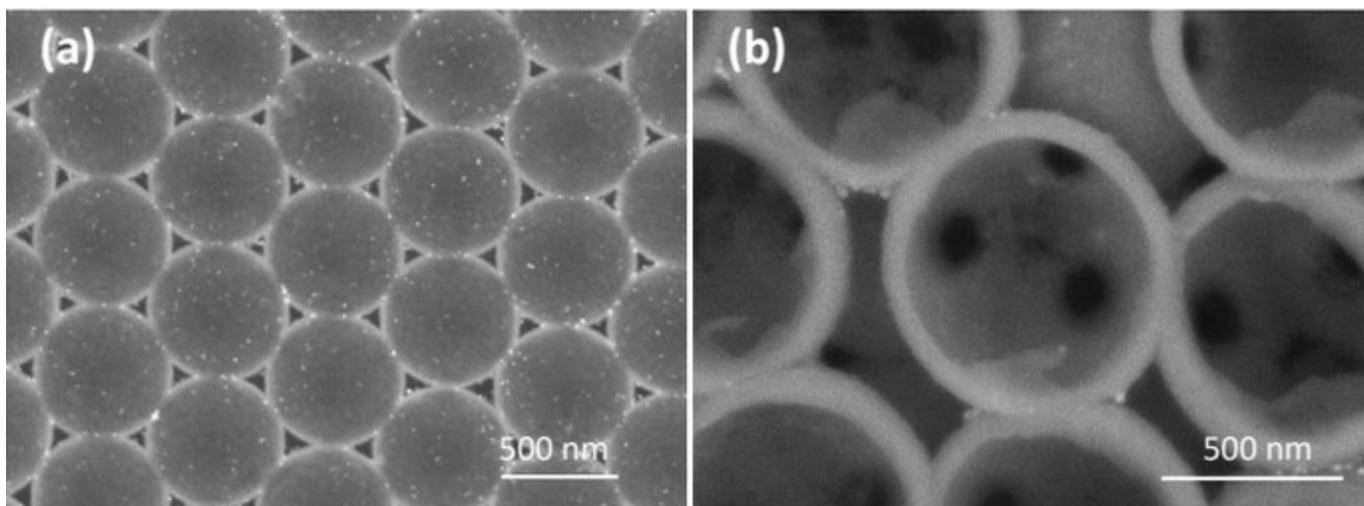


Fig. 1 – (a) SEM image of a Au-TiO₂ inverse opal film synthesized by ALD, (b) SEM image after ion polishing of the film for 2 minutes.

[1] L. Hu et al., *Catalysis Communications* 40 (2013) 106–110.

[2] S. W. Verbruggen, *J. Photochem. Photobiol. C-Photochem. Rev.* 24 (2015) 64–82.

Keywords

photocatalysis, inverse opals, atomic layer deposition, gold nanoparticles

03.19

Cobalt-based catalysts on zeolite supports for the ethanol steam reforming process: Tuning the catalyst properties towards desired reaction efficiency

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Abstract

Cobalt-based catalysts are widely studied for hydrogen production via the ethanol steam reforming process (ESR). The cobalt active phase is usually spread over a high surface area support e.g. Al₂O₃, CeO₂, or SiO₂. Zeolites with high porosity and a large specific surface area also seem to be interesting to support the ESR cobalt catalysts. Relatively little interest in these materials results from their high selectivity towards the highly undesirable product of ethanol dehydration path - C₂H₄. However, due to the very strong surface-structure-performance relationship, this path can be significantly reduced or even eliminated by a controlled modification of the zeolite properties.

The acidity of a zeolite catalytic system, mostly responsible for ethanol dehydration, can be modified in a wide range, either by doping with alkali or by decreasing the aluminum content in the structure. In our study, we evaluated the effectiveness of tuning the ESR performance using both these methods. A series of catalysts based on Y and ZSM-5 zeolites was synthesized, characterized (XRD, Raman Spectroscopy, UV-VIS, XPS, TEM/EDX, TG/DTA, TPR, and quantitative Py and CO adsorption FT-IR), and studied in the ESR process.

The strong effect of potassium on the catalyst performance was discussed in terms of potassium influence on the catalyst surface properties, most of all concentration and strength of the acidic Lewis sites. In addition, the results pointed out the significance of the potassium admixture speciation and location. However, the most spectacular results were obtained for catalysts based on zeolite ZSM-5 greatly depleted in aluminum or synthesized as pure silica zeolite. Such materials indicated outstanding performance: 100% ethanol conversion, high selectivity to desired products (e.g. S_{H₂} > 90%), and very high stability.

The work was financed by the National Science Centre, Poland, Grant No. 2021/05/X/ST5/00808.

KT acknowledges the financial support from National Science Centre, Poland, Grant No. 2020/37/B/ST4/01215.

Keywords

cobalt catalyst, zeolite, alkali addition, surface acidity

03.20

Effect of the substrate on the photoelectrochemical properties of ZnIn_2S_4

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Abstract

ZnIn_2S_4 (ZIS), as a representative of the group of ternary sulfides, is a promising material with photoelectrocatalytic properties towards water splitting due to its suitable arrangement of energy bands, sufficient ability to absorb visible light, and low environmental toxicity [1]. However, due to the strong recombination of charge carriers and the slow dynamics of surface oxygen evolution reactions, the performance of ZnIn_2S_4 as a photoanode is still not satisfactory. So far, many options have been described to enhance the performance of ZnIn_2S_4 as a photoanode, such as morphology modifications or deposition of other catalysts [2], [3]. Most works on the use of ZnIn_2S_4 as photoanodes describe layers of this compound deposited on FTO [4].

This study presents a comparison of the photoelectrochemical properties of ZnIn_2S_4 layers depending on the used substrate. ZnIn_2S_4 layers on FTO and TiO_2 nanotubes (TiO_2NT) were obtained using a hydrothermal process previously described in the literature [4]. 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 significant differences between the obtained photoanodes involve the generated photocurrents and their stability. FTO/ZIS photoanodes generated higher photocurrents of water oxidation during short-term illumination than $\text{TiO}_2\text{NT}/\text{ZnIn}_2\text{S}_4$. However, longer illumination under potentiostatic conditions (> 200 s), showed much higher stability of photocurrents generated by TiO_2NT -based photoanodes than those obtained using FTO.

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[2] W. Xu et al., Adv. Energy Mater., vol. 11, no. 8, pp. 1–8, 2021

[3] M. Zhou et al., Appl. Catal. B Environ., vol. 244, no. July 2018, pp. 188–196, 2019

[4] M. D. Sharma et al., Catal. Sci. Technol., vol. 9, no. 23, pp. 6769–6781, 2019

Keywords

photoanodes, water splitting, zinc indium sulfide, ternary sulfides

O4.01

Atomic layer etching of SiO₂ and TiN films with non-greenhouse gas of CF₃I

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Abstract

Atomic layer etching(ALE) with perfluorinated compounds(PFCs) is a promising etching technology based on sequential, self-limited surface reactions for metal oxide and metal nitride materials. However, PFCs generally have a high global warming potential(GWP), which is a significant figure of merit concerned with global warming. Therefore, in this work, plasma-enhanced ALEs of SiO₂ and TiN, important film in semiconductor device fabrication, were demonstrated through their surface modification by using non-greenhouse gas of CF₃I (GWP₁₀₀ = 0.3) and oxygen.

In ALE process of both SiO₂ and TiN, the self-limited and saturation characteristics of etch rate per cycle(EPC) was observed by varying the exposure time of each CF₃I and O₂ gas. In SiO₂ ALE process with plasma power of 300W, the EPC was 0.93 nm/cycle. In TiN ALE process, the EPC was modulated from 0.15 nm/cycle to 0.3 nm/cycle by only changing the O₂ plasma source power.

The ALE chemistry scheme for SiO₂ and TiN films was analyzed by using XPS tools. In SiO₂ ALE process, one cycle involved two steps: polymer deposition step and removal step. In the polymer deposition step, CF₃I plasma was treated on the SiO₂ surface to deposit fluorocarbon polymer. In the removal step, O₂ plasma was used to remove the deposited polymer. When fluorocarbon polymer was removed by O₂ plasma, SiO₂ film was etched by the byproduct of volatile SiF_x generated in the interlayer between fluorocarbon polymer and SiO₂.

In TiN ALE process, a cycle also consisted of two steps; oxidation and etching steps. In the oxidation step, the O₂ plasma oxidized the surface of the TiN film. In the etching step, the oxidized surface of TiN film reacted with F radical in CF₃I plasma. Then the oxidized TiN surficial layer was removed through a volatile byproduct of TiF₄.

Keywords

Atomic Layer Etching, CF₃I, Surface modification, Self-limited reaction

O4.02

Transition metal phosphates for electrochemical energy reactions.

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Abstract

The utilization of affordable and sustainable sources of energy has been a major worldwide concern, which has led to the implementation of several renewable energy systems in many developed countries. However, such systems are not enough to face the energy demand, and more advanced technologies are required. The use of hydrogen is an indispensable alternative to face the energy demand, as it can be obtained by splitting water in an electrolyzer (EL) and then be transformed into electricity in a fuel cell (FC). These processes involve catalyzed electrochemical reactions, in which the most efficient electrocatalysts are based on noble metals that are costly and scarce, and may assume up to 50% of the total devices' cost [1]. Thus, replacing noble metals with materials with lower cost, broader availability, and efficient electroactivity is crucial for implementing a real hydrogen economy.

Transition metal oxides have been widely studied as substitutes for noble metal electrocatalysts in EL and FC [2]. However, they present insufficient activity and long-term instability. Compared with transition metal oxides, ligand groups in transition metal phosphates exhibit flexible coordination and diverse orientations, making them very promising for designing highly active electrocatalysts. Therefore, this study proposes the use of $\text{Co}_x\text{Ni}_{3-x}\text{P}_2\text{O}_8$ ($0.0 \leq x \leq 3.0$) compositions synthesized via chemical co-precipitation as electrocatalysts [3]. The effect of replacing part of the Ni(II) by Co(II) in $\text{Ni}_3\text{P}_2\text{O}_8$ solid solutions has been studied. Compositions with higher Co(II) content exhibited a more stable polymorph structure similar to that observed in $\text{CO}_3\text{P}_2\text{O}_8$. It is expected that the phosphate group acts as the proton receptor to ensure the long-term stability of the electrocatalytic system and induce the distortion of the geometric structure of the metal to facilitate the adsorption of molecules promoting the electrochemical reactions.

Keywords

Electrocatalysts, Electrolyzers, Fuel cells, Hydrogen economy

O4.03

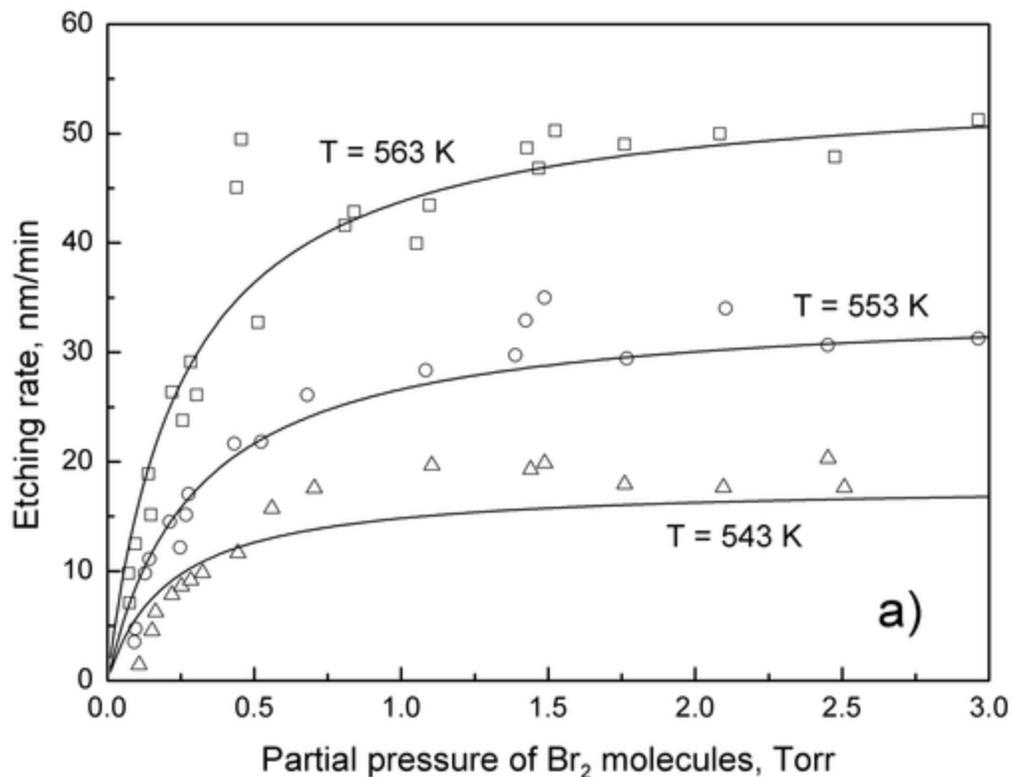
Michaelis–Menten kinetics during chemical etching of germanium

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Abstract

The chemical etching of germanium in Br_2 environment is investigated theoretically. The steady-state etching rate is described by the Michaelis–Menten equation. Experimental dependences of germanium etching rate on the partial pressure of Br_2 molecules are fitted to obtain reaction and desorption rate constants. The derived kinetic parameters are subsequently analyzed using the transition state theory. The determined activation energy of $\text{Ge(s)} + \text{Br}_2(\text{g}) \rightarrow \text{GeBr}_2(\text{a})$ reaction is equal to (1.168 ± 0.173) eV, and the desorption activation energy of GeBr_2 molecules is equal to (1.397 ± 0.014) eV. Surface passivation by the intermediate reaction product is not observed under the investigated experimental conditions.



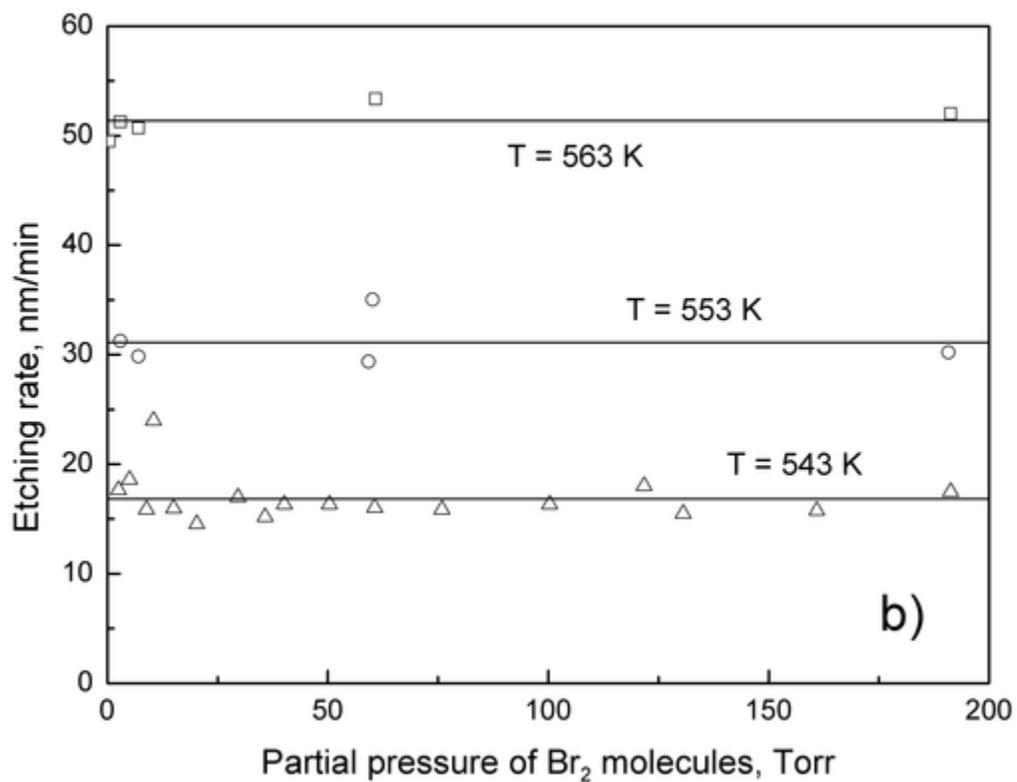


Fig. 1. The experimental and theoretical dependences of germanium etching rate on the partial pressure of Br₂ molecules.

Keywords

Germanium, Bromine, Chemical etching, Michaelis–Menten kinetics

O4.04

Novel transition metal aerogels synthesized by microwave heating

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Abstract

Nowadays, one of the great energy challenges is to supply the necessary energy for the entire world population via the cleanest and most efficient way to mitigate climate change. In long term, the solution must involve hydrogen fuel cells. These devices use the chemical energy of hydrogen to produce electricity without polluting subproducts, just water and heat (zero emissions). Nowadays, the most efficient catalytic materials used in fuel cells are based on noble metals, which are scarce and expensive. One of the lines of research carried out so far has been focused on the study of transition metals to decrease the cost. Transition metals are commonly supported on carbon materials, which may suffer oxidation due to the reaction conditions of the cell. The development of materials based on self-supported transition metals is an interesting strategy to face this drawback. The synthesis of nanoparticle aggregates with monodisperse nanopores, atomic layer deposition or nano-fluid systems, are some of the most common approaches. However, these processes require the use of templates. Accordingly, the development of a novel process to synthesise transition metal aerogels seem to be very promising.

This work presents the synthesis of iron aerogels obtained by microwave heating. The conditions of the synthesis process such as temperature, the ratio between reagents, and reaction time were modified to elucidate their effect on the formation of the structure. The microwave-assisted synthesis has reduced reaction times without influencing the structure. It has been observed that the most developed nanostructure is obtained by using a high metallic precursor/reducing solution ratio, and a temperature close to 90 °C. The transition metal aerogels obtained are highly promising as electrocatalysts in fuel cells, providing a high number of active centres that will improve cell performance.

Keywords

3D-nanostructure, sol-gel process, physicochemical properties, electrocatalysts

O4.05

The role of interfaces in hybrid/organic solar cells

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Abstract

Performance in PEDOT:PSS/silicon hybrid heterojunction PV devices is driven by the hybrid interface and degradation of this interface is characterized by the development of s-shaped JV responses. The impact of the degradation of the properties of the interfacial silicon oxide and the PEDOT:PSS film on the JV response of PV devices were simulated and fit to experimental results and found to be good predictors of the development of s-shape JV characteristics. X-ray photoelectron spectroscopy (XPS) showed that the interfacial silicon oxide develops rapidly after fabrication with a high concentration of suboxide defects that grows and chemically saturates to the native oxide thickness (1.5nm) and composition as the devices age. Hard X-ray photoelectron spectroscopy (HAXPES) was used to investigate the buried organic-silicon interface and showed that doping in the PEDOT:PSS backbone decreases and the PEDOT:PSS/silicon band alignment does not change measurably as the devices age. [1] Further electrical characterization showed that the metal/PEDOT:PSS interface was stable over the period of measurements, but the electrical properties of the PEDOT did change slightly.

Keywords

solar cells, interfaces, XPS, oxidation

O4.06

Identification of active sites on transition metal surfaces for the oxygen reduction and evolution reactions under reaction conditions

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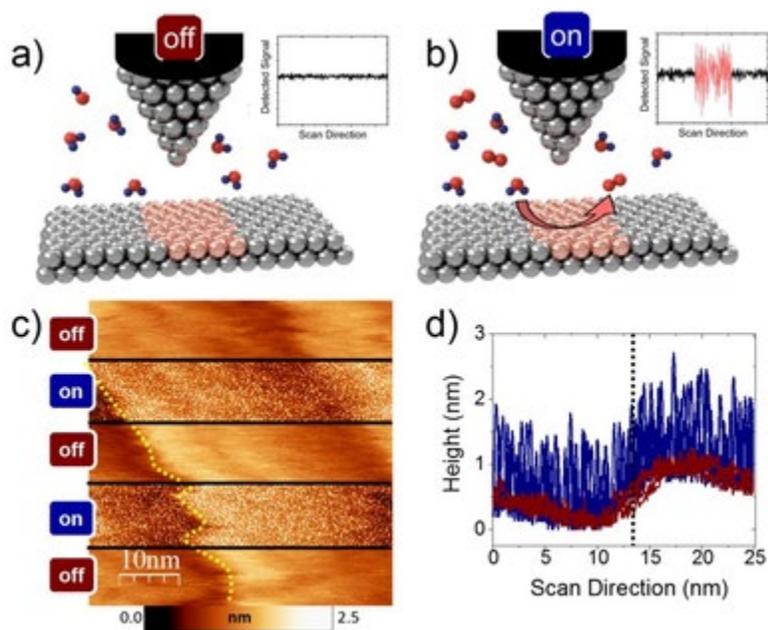
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Abstract

Electrochemical devices such as fuel cells and electrolyzers are among the key technologies on the route to a “green” way of energy provision and storage. However, their optimization requires an in-depth understanding of the electrochemical processes at the electrified solid/liquid interfaces. In-situ and in-operando techniques together with mathematical modelling are suitable to assess the conditions for optimal performance.

Electrochemical scanning tunneling microscopy (EC-STM) maps the electrode surface with a resolution down to the nanometer scale while allowing potential control. In the course of a reaction, continuous changes in the composition and structure of the tunneling medium lead to continuous changes in the tunneling barrier. Therefore, active sites can be identified by evaluating noise features in the STM signal.^[1] In Figures ab, the active sites are colored in rose, and spikes evolve in the signal under reaction conditions (“on”) unlike at less active sites.

An example of such a “noise” measurement on an IrO_x surface under oxygen evolution reaction (OER) conditions is shown in Figure c. An increased noise level can be seen when the reaction is switched “on” compared to “off”. In Figure d, height profiles in the scan direction across the step edge marked in c are given. When the OER is “on” (blue), multiple spikes can be seen in the STM signal compared to “off” (brown).^[2] This signal can be further evaluated to extract the local reactivity, e.g. of step edges and terrace sites. Moreover, platinum and its alloys for the oxygen reduction reaction are the content of this presentation.



Images c,d reprinted from reference [2]. © 2021 Elsevier Inc.

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- [2] R.M. Kluge, R.W. Haid, A.S. Bandarenka, *J. Catal* 396 (2021) 14-22.

Keywords

scanning tunneling microscopy, active site

O4.07

Roll-to-roll transferred cvd grown graphene/nafion composite membranes characterization for fuel cells applications

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Abstract

Our paper addresses an enormous need for more efficient energy systems such as fuel cells and electrolysers production based on 2D graphene. In this paper is investigated the influence of single and few (2-3) layers graphene grown by chemical vapor deposition (CVD) towards electrical and electrochemical performances of the modified Nafion 115[®]. The number of graphene layers was adjusted from 5 to 15 minutes time of reaction, using methane as carbon source during the CVD process on cooper foil substrate catalyst. The graphene transfer on the polymeric membrane was carried out using roll-to-roll method, by using a thermal release tape applied directly on the graphene layer. The increase of graphene layers deposited on the Nafion 115[®] was put in evidence by the decrease of transmittance obtained by UV-Vis spectroscopy. Further, Raman spectroscopy analysis, as well as scanning electron microscopy (SEM) were carried out to understand the structure of the samples. Moreover, there were obtained membranes with increased water uptake (WU), ion exchange capacity (IEC) and in plane proton conductivity measured by electrochemical impedance spectroscopy (EIS). At a temperature of 25°C and fully hydrated conditions, a value of 195 mS cm⁻¹ corresponding to composite membranes with graphene obtained after 11 minutes time of CVD growing, can be achieved. For higher graphene loadings, the proton conductivity decreases, which may be due to the excess amount of graphene, hindering and disrupting proton pathway.

Keywords

CVD Graphene, Membrane, Fuel Cell, Proton Conductivity

O4.09

Nickel-doped, niobium tungsten oxide nanowires as an anode material for lithium-ion batteries

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Abstract

Recently, niobium tungsten oxide nanowires have been reported as a promising anode material for lithium-ion batteries (LIBs). This material has demonstrated high theoretical capacity, significant structural stability, high power density, as well as environmental friendliness. Nonetheless, their low conductivity is a significant drawback that needs to be addressed. More so, it is desirable to enhance their electrochemical performance to meet the needs of current energy applications. In this study, pristine and nickel-doped (Ni = 1 wt.%, 3 wt.%, 5 wt.%) niobium tungsten oxide nanowires were fabricated using the electrospinning technique, followed by annealing. The effect of nickel doping content on the morphology, structure, and electrochemical performance of niobium tungsten oxide nanowires was investigated using X-ray photoelectron spectroscopy (XPS), X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), Raman spectroscopy, cyclic voltammetry (CV) and galvanostatic charge-discharge tests. The XRD results show that the incorporation of Ni into the structure of niobium tungsten oxide expanded the unit cell and enhanced the lithium-ion diffusion. The results of the electrochemical test indicate that the 3 wt.% Nickel-doped sample exhibits excellent electrochemical performance with high rate capability after 500 cycles at a high current rate of 5 C. Even when cycled at a high current rate of 10 C, the 3 wt.% Nickel-doped sample still delivered the highest initial reversible capacity compared to the other samples. Furthermore, the Ni doping significantly enhanced the electronic conductivity of the samples compared with the pristine niobium tungsten oxide nanowires. The results obtained from the CV test also show that doping nickel ions into the niobium tungsten oxide nanowires lowered the polarization and increased the lithium-ion diffusion coefficient. This study confirms that doping of niobium tungsten oxide nanowires with nickel significantly improved the electrochemical performance and electronic conductivity which is essential for future anode materials.

Keywords

niobium tungsten oxide nanowires , nickel doping , lithium-ion batteries , anode

O4.09

Copper fluoride growth on Cu(001): an STM, SR XPS and DFT study

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Abstract

The development of hybrid vehicles and portable devices requires improvement of high-energy batteries. So far, batteries operated by fluoride-ion shuttle in Cu/LaF₃-base have been reported [1], which calls for a thorough investigation of fluorine diffusion in copper and copper fluoride growth.

Recently, the fluorinated fullerene molecule has been proposed as a precursor of F-induced surface structures on copper [2]. The fluorinated fullerenes, adsorbed in submonolayer coverage, self assemble on the surface and gradually release the fluorine atoms.

We observed by STM the fluoride structures grown on Cu(001) crystal after adsorption of C₆₀F₄₈ molecule. The chemical states of fluorine and copper atoms were monitored by Cu2p and F1s signals of synchrotron radiation XPS. The stable structure with 2√2×√2R45 cell observed by STM is identified as a missing row structure of two-dimensional cuprous fluoride. The XPS Cu2p spectrum clearly indicates a Cu(I) oxidation state on the surface and the corresponding F1s line displays a low binding energy of 683 eV. The model of the surface fluoride structure is supported by DFT calculations which are in good agreement with STM image contrast. Under higher fluorine concentration the surface fluoride transforms into stable CuF₂. The Cu(II) fluoride is characterized by final state splitting of the Cu2p spectrum and a shift of the F1s line to 684 eV. The theoretical modelling of the surface Cu(II) fluoride in terms of rutile structure is discussed.

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Keywords

fluorination, copper fluoride, STM, XPS, DFT

O4.10

Influence of Er activator and Yb sensitizer on photoelectrochemical performance of TiO₂ thin film

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Abstract

Titanium dioxide photoanodes exhibit limited efficiency within the visible range of the light spectrum due to their inability to absorb the sub-band photons. To overcome this problem, an unconventional approach based on nonlinear up-conversion (UC) process has been proposed. It consists in harvesting of two or more infrared photons contributing to emission of one UV photon that can be absorbed by the wide-band-gap TiO₂. As we have already demonstrated [Kot A., Radecka M., Dorosz D., Zakrzewska K., Optically Active TiO₂:Er Thin Films Deposited by Magnetron Sputtering, *Materials* 2021, 14, 4085] the UC occurs in TiO₂:Er.

UC materials are usually composed of an activator embedded in a host and often a sensitizer. Here, to achieve efficient UC, two strategies are applied: 1) introduction of high content of activator (Er³⁺); 2) incorporation of low content of activator with addition of sensitizer (Yb³⁺).

TiO₂:Er,Yb thin film photoanodes have been deposited by reactive radio frequency magnetron sputtering from metallic Ti/Er (90/10 at.%), Ti/Er/Yb (98/1/1 at.%), and Ti/Er/Yb (88/2/10 at.%) targets in gas atmosphere with intentionally varied O₂/Ar ratio. Effect of Er³⁺ and Yb³⁺ on TiO₂ phase composition, optical properties, microstructure and photoelectrochemical properties has been investigated by means of X-ray diffraction, UV-VIS-NIR spectrophotometry, scanning electron microscopy, and current-voltage measurements.

TiO₂:Er,Yb films with low content of rare earth RE ions are well-crystalized and their phase composition changes from rutile to rutile-anatase mixture as O₂/Ar ratio increases. Higher concentrations of RE ions strongly affect TiO₂ structure leading to amorphization. However, the short-range order cannot be excluded. Amorphization and embedding of RE ions shift the band gap of TiO₂ to higher energies.

Our aim is to show an impact of activator (Er³⁺) and sensitizer (Yb³⁺) ions on photoanodes properties and their photoelectrochemical responses to illumination.

EU Project POWR.03.02.00-00-I004/16 is acknowledged by AK.

Keywords

TiO₂ thin film photoanodes, erbium, magnetron sputtering, water splitting

O4.11

Influence of hygroscopic salt incorporation in nanoporous materials for thermochemical heat storage application

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Abstract

Solar energy is one of the most promising types of renewable energy thanks to its high availability and low cost [1]. Energy storage systems have therefore been developed in order to reduce the discrepancy between demand and supply. In particular, thermochemical heat storage systems using reversible sorption/desorption reactions, offer high energy storage density over variable amounts of time with minimal heat losses. Water sorption storage systems using hygroscopic salts, such as CaCl_2 , inside a porous matrix are widely used [2]. These composite materials allow the storage of energy (solar or from any other source) during dehydration (charge) and its release during hydration (discharge). Metal-Organic-Frameworks (MOFs) have recently been of particular interest because of their high sorption capacity due to a very high surface area and tunable properties [3].

This work reports a study of heat storage/release and water sorption/desorption capacity of composite materials. Materials were subjected to analysis by TG-DSC coupled to a humidity generator during successive hydration/dehydration cycles. A first serie of materials based on aluminum fumarate MOF impregnated by different amounts of CaCl_2 (25,37 and 58 wt.%) were synthesized. DSC analysis showed that after salt incorporation, the heat storage/release capacity of MOFs gradually increases with the amount of salt reaching 1840 kJ kg^{-1} for AF- Ca_3 sample (AF + 58 wt.% of CaCl_2). A concomitant increase in water sorption/desorption capacity, determined by thermogravimetric analysis is observed. Besides, the presence of highly hygroscopic CaCl_2 enhances the surface affinity for water and hydrophilicity of composites, leading to a faster sorption rate.

The storage properties of a second serie of materials based on aluminum fumarate membrane on alumina support with a different morphology from aluminum fumarate have also been studied. The remarkable storage capacities of these new materials give them a significant place in the energy challenge.

Keywords

Thermochemical heat storage, hydrophilicity/hydrophobicity, MOF, Calorimetry

O4.12

The passivating effect of ionic liquids on mixed-cation perovskites investigated with in-situ near-ambient pressure X-ray photoelectron spectroscopy

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Abstract

X-ray photoelectron spectroscopy (XPS) is an ideal technique to investigate surface and interface reactions. However, the investigation of the material in atmospheric conditions is restricted by the requirement of high vacuum conditions. Therefore, near-ambient pressure XPS (NAP-XPS) has emerged as a powerful tool to study surface reactions in gaseous environments [1].

The long-term stability of mixed-cation perovskites is considerably improved when ionic liquid (IL) is added to the perovskite precursor [2]. The stability of $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ (FACs) is improved by (0.3 mol%) of 1-octyl-3-methylimidazolium chloride. Therefore, understanding the role of this ionic liquid in improving stability is of high interest. Here, the degradation of perovskite compositions grown with and without addition of IL is investigated by XPS and NAP-XPS techniques. Heat-induced degradation at different temperatures (100 and 150 °C) was investigated with XPS under UHV conditions. Moisture-induced degradation was investigated with NAP-XPS in the presence of 9 mbar conditions. In addition, simultaneous heat- (100 and 150 °C) & moisture-induced degradation were investigated with NAP-XPS under 9 mbar of water pressure.

We demonstrate that FACs decomposes into metallic Pb and leaving PbI_2 on the surface upon heating with the loss of iodine, but, the presence of ionic liquid in the sample inhibits the loss of organic cation from the lattice due to an accumulation of IL molecules on the surface. However, the IL-FACs sample undergoes decomposition at 150 °C under humid conditions. Interestingly, no chemical changes were observed at room temperature under 9 mbar water conditions, which indicates that heat and moisture together induces the decomposition of IL-FACs, rather than moisture or heat alone. The result illustrates the importance of passivating or encapsulating the material surface to make a stable material system.

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[2] S. Bai et al., Nature, 2019, 571, 245-250.

Keywords

mixed-cation perovskite, ionic liquid additive, stability, near-ambient pressure X-ray photoelectron spectroscopy

O4.14

Effect of differing Si/Al on the adsorption and separation of CH₄/CO₂ over Na-CHA zeolites

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Abstract

In this work, several Na-exchanged commercially available CHA zeolite materials (Si/Al ratios 8 – 16) were studied as potential adsorbents for the separation of CO₂/CH₄ mixtures. Their separation performance was evaluated by measurement of single-component volumetric adsorption isotherms of CO₂ and CH₄ and subsequent analysis of the data by numerical methods (IAST, calculation of adsorption enthalpy). It was found that the uptake of CO₂ and ideal selectivity of CO₂/CH₄ on Na-CHA materials depend significantly on the Si/Al ratio, with the material Na-CHA-8 showing slightly better CO₂/CH₄ ideal selectivity and comparable uptake as the benchmark 13X zeolite material, as well as slightly lower values of the adsorption heats (by about 4-5 kJ/mol), as reported in literature, suggesting a potential lower cost for the regeneration of the adsorbent. In order to shed more light into the interaction of CO₂ with Na-CHA, variable pressure (0 – 1.5 mbar) FTIR spectroscopy was used. Three vibrational bands (2365, 2355 and 2348 cm⁻¹) were observed in the region of the CO₂ asymmetric stretch mode, corresponding to CO₂ molecules interacting simultaneously with two Na⁺ cations (dual-site) - band at 2365 cm⁻¹ and CO₂ molecules interacting with two differently coordinated Na⁺ cation single-sites (a more stable band at 2355 cm⁻¹ and a less stable band at 2348 cm⁻¹). Different distribution of the site population was observed with differing Si/Al ratio, the strength of the band corresponding to the dual-sites correlating with low pressure CO₂ uptake, as well as selectivity. It should be pointed out, that complete desorption of CO₂ molecules at ambient temperature, as observed by FTIR spectroscopy, was achieved in 2-3 min under dynamic vacuum for all studied samples, further suggesting a low energy cost of regeneration of the adsorbents.

Keywords

Adsorption, Separation, Chabazite, Carbon dioxide

O4.15

Regeneration and recombination kinetics in Dye Sensitized Solar Cell: Cation concentration and potential control

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Abstract

The Dye Sensitized Solar Cells (DSSCs, Fig. 1) are promising candidates for the low-cost photovoltaics, sensitive to the low intensity and diffuse light(1). The possibility of the transparent configurations is an advantage for the development of the building integrated photovoltaics. To improve the efficiency and stability of these devices, the investigations of the regeneration and recombination processes were performed.

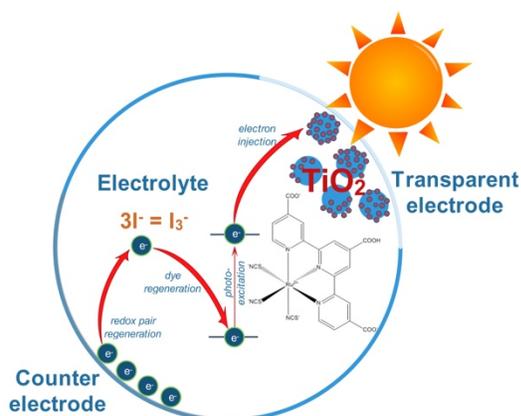


Figure 1 DSSC schematic representation

After the absorption of light by the photosensitizer, the electron injection from the excited state into the TiO_2 conduction band occurs and the photosensitizer cation is formed. The cation is then regenerated by the redox couple present in the electrolyte. However, a parallel process of the recombination of the electron in TiO_2 with the cation takes place and thus a fraction of the absorbed light is wasted. These processes were studied, using nanosecond transient absorption spectroscopy for two emblematic photosensitizers: C106 (ruthenium dye), C218 (organic).

Although the processes of regeneration and recombination were found to follow non-first order kinetics, the regeneration efficiency is independent on the concentration of the cation initially generated by a short optic pulse. The kinetics of the regeneration was shown to be dependent on the electrostatic potential applied to the DSSC device during the nanosecond TA measurements (Figure 2).

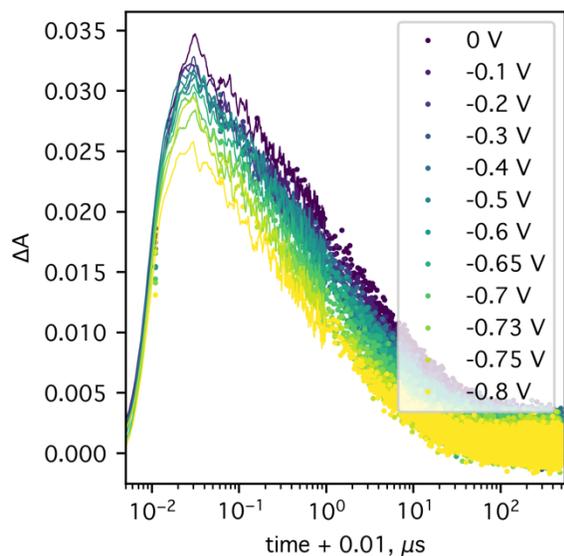


Figure 2 C106 cation absorbance decays, obtained using 580 nm light excitation and recorded at 760 nm. Electrostatic potential was applied using a potentiostat. Bias white light of circa 1 Sun was applied.

Kinetic theories for the mechanisms of these processes(2, 3) are proposed and tested for the experiments with different applied bias potential and different concentrations of the generated cations.

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Keywords

dssc, nanosecond transient absorption

O4.16

Metal-free electrodes based on nitrogen-doped carbon cloth as electrocatalysts for water-splitting reactions

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Abstract

In recent years, hydrogen has been recognized as a promising clean energy vector for the future because of its high energy density per unit mass and the possibility of facile production from the electrolysis of the renewable feedstock- water. Nevertheless, current electrolyzers suffer from high energy consumption resulting from high overpotentials of hydrogen and oxygen evolution reactions, which take place simultaneously during water splitting. This issue can be fixed by the application of proper electrocatalytic materials. Therefore, there is an urgent need to find low-cost, highly active and stable electrocatalysts.

In this work, metal-free electrocatalysts were prepared by an easy to perform two-step modification of the carbon cloth. The modification procedure was separately optimised toward the formation of active and stable electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). In both cases, the procedure involved two steps – carbon cloth oxidation (mild in the case of OER and substantial for HER) and following thermal treatment in ammonia flow. The combined treatments resulted in carbon cloth surface doping with nitrogen. The physicochemical properties of the materials were characterised using XPS, Raman, SEM and TEM techniques and their electrochemical and electrocatalytic performances were assessed by LSV, CV, EIS and chronoamperometry. The optimisation resulted in obtaining the electrodes that catalysed the OER and HER with overpotentials of 390 mV and 325 mV, respectively, at +/- 10 mA cm⁻² in 1.0 M KOH. These electrodes were also applied to a model alkaline electrolyser as an anode and a cathode, respectively.

The results suggest that the highest electrocatalytic performances toward HER are achieved using materials with moderate heteroatom concentrations on the surface and low content of structural defects in the carbon material. On the other hand, OER stability during performance requires the application of material with high ordering of the carbon structure.

Keywords

hydrogen evolution reaction, carbon cloth, water splitting, electrocatalyst

O4.17

A two-source XPS study of highly orientated pyrolytic graphite implanted with cesium ions.

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Abstract

A sample of HOPG was implanted with Cs⁺ ions in order to study the effect on the graphite matrix and, importantly, the chemical form of the Cs species once embedded. The mean implantation depth was found to be ~ 22 nm, allowing for investigation via XPS, where both a traditional Al K α X-ray source and a higher energy Ag L α source was used for enhanced depth resolution. Analysis of the measured spectra found that there was a reduction of sp^2 C-C bonding with implantation dose, with a total loss of sp^2 character at ~ 6 at% Cs⁺. A striking increase in higher BE components (285.8 – 289.4 eV) in the C 1s spectra cannot be attributed solely to the presence of C-O species, instead indicating a dramatic re-ordering of the graphitic lattice, to accommodate and neutralize the embedded Cs. XPS analysis of the O 1s and Cs 3d spectra suggest the formation of cesium carbonate within the graphitic material and this conclusion is reinforced by analysis of a Cs₂CO₃ reference sample.

Keywords

high-energy XPS, ion implantation, chemical speciation, nuclear

O4.18

XPS surface characterisation of novel Li solid electrolyte energy storage materials

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Abstract

Lithium ion batteries are commonly found in home electronic equipment. In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. In the past few years, there has been an explosion of interest in solid-state lithium-ion batteries, which are a promising technology to replace conventional liquid electrolyte lithium ion cells because of their much greater intrinsic safety. As in all batteries, however, the chemistry and stability of the electrode- electrolyte interface is critical to the performance of the device.

Here we will apply XPS depth profiling techniques to determine elemental composition and the chemical/electronic structures below the surface of ALD grown LiPON thin-films. Depth profiling has been used across on broad range of materials however the method has been shown to induce preferential sputtering and other chemical artefacts. More recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials and broaden the range of materials amenable to this type of analysis. Here we extend the application of cluster ions beyond organics to inorganic materials. We will demonstrate how, with the use of high energy $\text{Ar}_{250-3000}^+$ ions, it is possible to obtain more accurate surface and interface information regarding the true chemical nature of LiPON thin-films. A comparison is made with conventional Ar^+ monatomic depth profiles in particular the differences in stoichiometry obtained with the two ion sources. Ion implantation and migration is also discussed as are the unfortunate chemical effects of carbon deposition from organic cluster ions.

Keywords

XPS, Batteries, Cluster ions, solid state

O4.19

An experimental investigations of structure - activity relationships for model catalytic systems

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Abstract

The most frequently used catalysts in fuel cells are nanoparticles of Pt or Pt alloy, deposited on carbon black. These systems operate in harsh conditions, especially during start-up and shutdown, when the potential can reach values up to 1.5 V, leading to catalyst degradation. The degradation mechanism is varied. At high potentials, the carbon support is thermodynamically driven to be oxidized. Dissolution, particle coalescence and Ostwald ripening are responsible for the degradation of platinum nanoparticles. Particle detachment is also possible from the carbon support. Obtaining better catalytic systems requires the control of their microstructure (particle size, morphology, electron and crystal structure, surface shape) and chemical composition. Transmission Electron Microscopy TEM is one of the most powerful techniques (in some cases the only one) that allows to do this task with the expected space resolution. The question is, would electron microscopy be useful in answering the question: how to improve the durability of catalysts? To assess durability and explain why the catalyst activity decreases, we monitor evolution of electrocatalysts during accelerated fatigue tests. Our efforts focus on explaining changes in the structure of the catalytic system (platinum nanoparticles and carbon-based support) during use, by comparing the structure of a precisely located catalyst fragment (IL-TEM identical localization technique) before and after testing. The IL-TEM measurements are correlated with the results of electrochemical and structural studies. Such observations may explain why the activity of the catalyst decreases and what could be proposed to reduce this effect.

Keywords

fuel cell catalyst, platinum nanoparticles, degradation mechanisms, stability

O4.20

Binder-free TiO₂ nanotubes/MoS_x/MoO₃ electrode material for energy storage applications: surface design and electrochemical performance

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Abstract

In this study, a binder-free TiO₂ nanotubes/MoS_x/MoO₃ electrode material was synthesized through a hydrothermal route. The aim of this research was to investigate the influence of the concentration of hydrochloric acid used in hydrothermal synthesis on the surface architecture and electrochemical performance of the electrode material with application in supercapacitors. When the concentration was low, the formation of nanostructures was not observed, while at higher concentrations, structures in the form of cubes, spheres, or flocs can be distinguished. The obtained results indicate that various concentrations of hydrochloric acid led to significant differences in surface appearance and thus to the overall performance of the electrode material in energy storage applications.

The research also focused on differentiating capacitances on the basis of Conway's approach [1], as well as one that was proposed by Trasatti and co-workers [2,3]. The estimation of the contributions of "inner" surface and "outer" surface to the total charge measured using voltammetry has been performed. The electrode material was also tested for long-term cycling stability through galvanostatic charge/discharge tests in 1M H₂SO₄. After 10 000 cycles, the TiO₂ nanotubes/MoS_x/MoO₃ electrode material was characterized by a coulombic efficiency at almost 100% and the areal capacitance value of 240 mF cm⁻².

Acknowledgments

This research was funded by the National Centre for Research and Development via Grant No. LIDER/15/0088/L-10/18/NCBR/2019.

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Keywords

energy storage, supercapacitors, molybdenum sulfide, hydrothermal synthesis

O5.01

Work function of the oxygen functionalized graphenic surfaces – integral experimental and theoretical approach

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Abstract

The effect of oxygen plasma functionalization of graphenic surface was thoroughly investigated experimentally (XRD, SEM, XPS, Raman spectroscopy, work function measurements) and corroborated by DFT molecular modeling using periodic slab models (work function, surface dipoles, E_F /DOS). It was found that the introduction of oxygen substantially modified the electrodonor properties of the graphenic surface and the work function changed in a non-monotonous way upon the plasma treatment time. At the short contact time (5-30 s) the work function significantly increased from 4.2 eV (parent graphenic surface) to 5.6 eV and after passing the maximum value, after 100-150 s stabilized at the level of 5.2 eV. The XPS revealed that the plasma treatment leads to an increase in oxygen surface concentration (up to ~10 at.%). Comparison of SEM images and Raman spectra of unmodified and plasma-modified graphenic surfaces indicated that the induced changes are limited to the outermost surface. Indeed, the XRD results and TG/DTA stability profiles did not indicate any bulk structural changes. Based on the experimental and DFT results, the molecular model of the surface modification process was proposed taking into account the various location of surface oxygen functionalities. At the early stage of the plasma treatment, a generation of strongly polar surface functional groups (surf-OH with a the dipole moment of 2.7 D) leads to the formation of an electrostatic potential barrier for electron transfer from the surface (observed increase in work function). Prolonging modification leads to the insertion of oxygen heteroatoms into the carbon surface resulting in a more uniform electron density distribution and work function decrease. Since the electronic properties of graphenic materials play a key role in their various applications, the obtained results provide rational guidelines for their design and optimization.

This study was supported by the National Science Centre, grant no 2020/ 37/B/ST5/03451.

Keywords

graphenic surface, work function, oxygen plasma, DFT calculations

O5.02

Unraveling the role of support membrane chemistry and pore properties on the formation of thin-film composite polyamide membranes

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Abstract

Nanoscale characteristics of the polyamide layer are key towards the high desalination performance of thin-film composite reverse osmosis (TFC-RO) membranes. Further advancements in the performance of TFC membranes necessitate a comprehensive understanding of the desired polyamide characteristics and its formation mechanisms. Empirical evidence has shown that the properties of the support layer is as equally important as the interfacial polymerization (IP) conditions in the fabrication of high permselectivity TFC membranes for desalination. Herein, we discuss the properties of polyamide layers formed using identical IP conditions over support membranes of different polymers and chemistries (polyethersulfone, polyetherimide and polysulfone) under fairly similar surface pore properties. The characteristics of the polyamide layers formed thereon displayed different physicochemical properties. It is postulated that the support membrane chemistry actually affects the IP reaction and polyamide formation by controlling the amine diffusion speed as well as the breadth of the IP reaction zone (*i.e.*, the region between the interface and the furthest point in which the reaction occurs). Transmission electron microscopy analyses further revealed the nanoscale differences in the polyamide layer (heights ranging from 50-200 nm), including intrinsic thickness of basal layer (~10-35 nm) and leaf-like top layer (~20-85 nm), as well as the presence of nanovoids. Finally, we propose a conceptual model to underline the role of support membrane chemistry in the IP reaction, and consequently the formation mechanism of the nanoscale polyamide features. The mechanistic insights from this study are expected to provide more understanding towards a better control over the fabrication of polyamide layers for TFC membranes. The findings in this work are also expected to facilitate tailoring polyamide layers for specific osmotically driven processes.

Keywords

Thin-film composite membrane, support membrane chemistry, interfacial polymerization

O5.03

Functionalization of SBA-15 mesoporous silica with amine and thiol for highly efficient adsorption of glutathione from aqueous solutions: characterization and modeling studies.

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Abstract

SBA-15 mesoporous materials were prepared using an amphiphilic triblock copolymer (P123) as a template and tetraethylorthosilicate (TEOS) as a silica source under acidic medium according to the method described by [1]. Then, the materials were functionalized with either 3-(aminopropyl)triethoxysilane (APTS) or 3-mercaptopropyltriethoxysilane (MPTMS) in order to introduce amine or thiol groups onto the surface by using a post-grafting method. The functionalized materials (SBA-15-NH₂ and SBA-15-SH, respectively) were characterized by FTIR, TGA, XPS, SEM and TEM. Then, the as-prepared materials were used as adsorbent for the adsorption of glutathione (GSH) molecules from aqueous solutions. Nevertheless, the adsorption capacities of glutathione (GSH) molecules of the SBA-15-based materials were studied after each step, and it was shown that the contact time and the initial GSH concentration significantly affect their adsorption capacities. In particular, it was shown that the maximum adsorption capacities of the SBA-15-NH₂ adsorbent were as high as $1.940 \pm 0.054 \text{ mmol.g}^{-1}$ for GSH molecules under optimal experimental conditions (GSH concentration=10 mg.L⁻¹, pH=7 and T=293 K). To examine the underlying mechanism of the adsorption process, pseudo first order, pseudo-second order, Elovich, Aharoni, interparticle diffusion models were fitted to experimental kinetic data. It was shown that the pseudo-second-order model was appropriate to describe the adsorption of GSH molecules by SBA-15-SH and SBA-15-NH₂ solid materials. Furthermore, the Freundlich, Langmuir and Harkin-Jura approaches analyzed adsorption data. Moreover, adsorption thermodynamics of GSH molecules have been studied at various temperatures and confirmed the endothermic adsorption nature of the adsorption process onto the SBA-15-SH adsorbent.

Keywords

SBA-15-based materials, Characterization, Adsorption, glutathione

O5.04

Photoelectric and sensing properties of SnO₂ infrared transparent conducting films

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Abstract

Tin oxide (SnO₂) has been widely explored for various applications due to its excellent n-type semiconductor properties, low resistance, and high optical transparency in the visible range. However, few studies on the preparation of SnO₂ films using high power pulsed magnetron sputtering have been reported. Oxygen content is a critical parameter in the practice of SnO₂ thin films by high-power pulsed magnetron sputtering. the average free range of Sn atoms is usually much smaller than O atoms. SnO₂ films deposited in a pure Ar atmosphere are likely to be oxygen-deficient and form O vacancies. and such oxygen vacancies will cause lattice distortion, which will affect the mobility and concentration of charge carriers in the SnO₂ film. According to Drude's model, the carrier concentration is closely related to the resonance of infrared photons.

In this paper, the crystal structure and infrared transparent conductive properties of SnO₂ films prepared at 600°C were investigated at different oxygen partial pressures. Then, it is described that integrating SnO₂ transparent conductive film into a multi-resonant surface enhanced infrared absorption (SEIRA) platform can overcome the shortcomings of poor selectivity and opacity of multi-gas sensing, and can simultaneously sense ultra-low concentrations of greenhouse gases on-chip. And realize the application in the transparent window scene. This strategy takes advantage of the near-field intensity enhancement of the multi-resonance SEIRA technology and the infrared light reflectivity that can be modulated by the SnO₂ infrared transparent conductive film. Experiments have proved that the platform realizes synchronous on-chip sensing of VOCs, with fast response time, high accuracy, high visible light transparency, and excellent linearity in a wide concentration range. In addition, the excellent scalability to detect more gases was explored.

Keywords

SnO₂, Infrared Transparent Conducting, Sensor, LSPR

O5.05

Advanced surface FTIR spectroscopy for the characterization of block copolymer coatings

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Abstract

Characterization of polymers and copolymers coatings requires the use of dedicated techniques. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) is an innovative and original vibrational spectroscopy used for "in situ" reflectivity experiments to characterize polymers and copolymers coatings deposited on reflective substrates. Due to the polarization modulation of the incident IR wave and surface selection rules, its reflection at the interface increases the sensitivity of the spectral response, allowing determination of molecular orientation and structuring effects. This work focuses on the understanding on how crystallinity of homopolymer or copolymer is modified in thin films and how this organization can be directed by the surface chemistry of the metal substrate.

Homopolymers and copolymers were spin-coated on metal substrates. The surface chemistry of the substrate was controlled by chemical grafting using thiols. The influence of the hydrophilic or hydrophobic surface of the substrate on the organization and structuration of homopolymers and copolymers of different compositions was then studied. Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between polymer/polymer and polymer/substrate interactions, which will have a direct effect on the crystallization.

This was explained by changes in the balance of polymer/polymer vs polymer/substrate interactions. Substrate surface chemistry drives the balance between these interactions. As an example, in the case of amphiphilic di-block copolymers, hydrophilic substrate favors the crystallization of the polar block whereas hydrophobic substrate will favor the non-polar block crystallization. The modification of the crystalline phase content, morphology and molecular orientation of the crystalline structures of the adsorbed films reflects the strong competition between interfacial forces and intra and intermolecular forces. Atomic Force Microscopy (AFM) analyses were also performed on coatings in order to access the surface morphology and to distinguish the polymer amorphous and crystalline phases.

Keywords

Surface spectroscopy, PM-IRRAS, Block copolymers, Coatings

O5.06

On the effect of H₂ and O₂ impurities on work function of cesiated Mo(001): A detailed DFT investigation

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Abstract

At usual operating conditions of hydrogen ion production systems based on the ionization process, the surface of converter is inevitably exposed to impurities, such as H₂O, H₂ and O₂. Since the presence of impurities is likely to affect the work function of the converter material, whose value has a strong impact on the efficiency of the electron extraction process, a detailed understanding of the fate of impurities upon their adsorption is essential for a rational design of efficient H⁻ sources. In this work, we address this problem by means of ab initio DFT simulations that provide us with atomic level details on the distribution of impurities and enable us to infer the effect of impurities on the work function of the material. As a model system, we chose the Mo(001) surface with several different sub-monolayer and multilayer Cs depositions interacting with impurities H₂ and O₂. Regardless of the Cs coverage, a full dissociation of the impurity molecule into its atomic constituents is found to be the dominant adsorption scenario. The most favorable sites available for adsorption are located on the Mo substrate, i.e., underneath the Cs deposition. However, if these sites are not accessible, e.g., due to kinetic limitations, the impurities will adsorb with a greatest likelihood on the sites close to the uppermost Cs layer. As we shall thoroughly discuss, the factors, such as the Cs coverage, electronegativity of adsorbate, its position within the substrate, or the adsorption-induced modifications of the substrate structure, give rise to a rather a complex changes in the work function induced by the impurity adsorption.

Keywords

DFT, work function, adsorption, negative hydrogen ions

O5.07

Hybrid three-dimensional structures with a high aspect ratio in the form of an array of silicon nanowires with deposited silver nanoparticles by the plasma enhanced atomic layer deposition method.

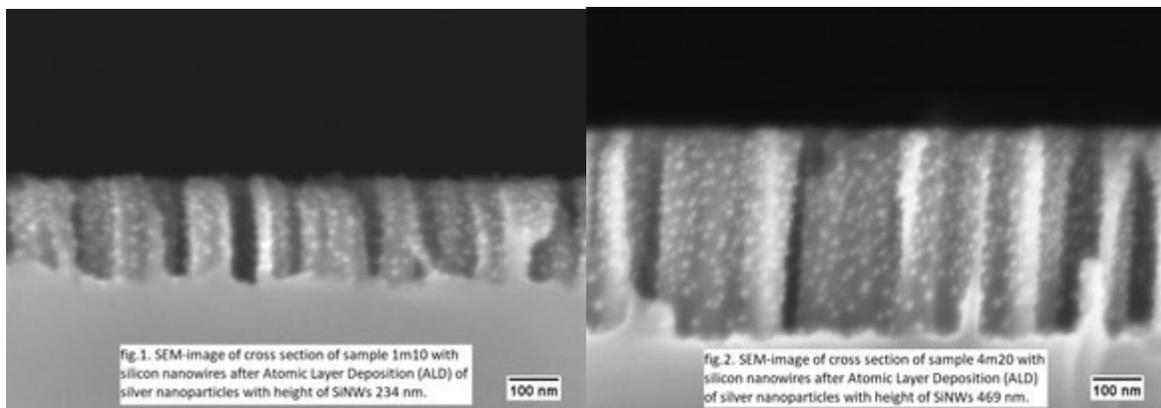
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Abstract

For creating structures with fundamentally new properties, hybrid silicon structures are widely used. Preliminary calculations showed the presence of localized plasmon resonances (LPR) from the Si:Ag composite layer not only in the visible region of the spectrum, but also in the near-IR range, which is important for various of applications. The creation of structures with a large specific surface area in the form of vertical Si nanowires (SiNWs) and with precision deposition of metal nanoparticles on them will make it possible to obtain new composite structures with a controllable position of LPR. Arrays of silicon nanowires, with a height of 100-500 nm and a cross-section of nanowires from 20-50 nm, were fabricated on a Si substrate by metal-assisted chemical etching. Atomic layer deposition (ALD) was used to deposit Ag nanoparticles (AgNPs). Analysis of the morphology showed a uniform coating of SiNWs with AgNPs along the entire height (fig.1, 2). Using optical methods (spectroellipsometry, polarization spectrophotometry) we observed a shift of the optical spectra in the array of Ag:SiNWs, and using the effective medium model, we revealed a nonuniform optical profile of the nanowires and determined the volume fractions Ag (f_{Ag}) and Si (f_{Si}) depending on their height: from 0.01 and 0.74 in the lower part of the SiNWs, and 0.024 and 0.13 in the upper part.

The calculation of the distribution of the electromagnetic field by the finite element method in COMSOL Multiphysics showed "hot spots" at the surface of AgNPs, the detected strong localization of the electromagnetic field should enhance the optical response of the Raman scattering. COMSOL simulations of the electromagnetic fields of AgNPs on a Si showed a Raman enhancement factor of $1,7 \cdot 10^5$. Due to the high concentration of plasmonic nanoparticles in the volume of the SiNWs, a significant increase in Raman scattering is expected.



Keywords

Atomic layer deposition, Silicon nanowires and Ag nanoparticles, Localized plasmon resonance, Spectroscopic ellipsometry

O5.08

Heterogeneous freezing and ice adhesion on charged surfaces

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Abstract

Controlling the heterogeneous ice nucleation and ice adhesion has many attractive applications in the pharmaceutical and food industry as well as for anti-ice surfaces in the energy and infrastructure sector. There is an ongoing discussion to what extent electric fields and charged surfaces affect the ice build-up and removability. [CAR15, JHA17, APE20]

Surface charges might influence the hydrogen bonding and water molecule orientation in the electrochemical double layer at the solid-liquid interface and therefore the ice formation and adhesion. It is well-known that the adhesion of ice can be explained based on a so-called quasi liquid layer (QLL) at the solid-ice interface. The temperature, roughness and ion content of the solid-liquid system strongly affects the effectivity of this layer for easy ice-removal. The effect of electric fields and surface charges on the structure of the QLL is not yet known.

Polished aluminium is the most wide-spread reference material for the development of anti-ice coatings. In order to achieve charged aluminium surfaces, the pH value of the liquid phase was varied from 3 to 10. Positive surface charges up to $20 \mu\text{C cm}^{-2}$ build up for pH values below the point of zero charge (pH_{PZC} of Aluminium ~ 8) and negative for pH values above the pH_{PZC} , respectively. Experimental results for the effect of positively and negatively charged surfaces on the contact angle, the heterogeneous freezing temperature and the ice adhesion strength will be presented and discussed.

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Keywords

anti-ice, electrochemical double layer, quasi liquid layer

05.09

The effect of oxidation of p-type copper halides films fabricated by pulsed laser deposition

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Abstract

Transparent electronics is a fast-growing research area with a wide range of everyday device applications. Conventionally used wide bandgap semiconductors such as ZnO are mostly of n-type conductivity. However, there is a lack of suitable p-type transparent oxide semiconductor materials with high conductivity and high optical transparency. In recent years a special interest was given to the development of p-type semiconductors-based copper halides due to their exceptional optical and electrical properties. In presented work we report the fabrication of the CuI and CuBr thin films by Pulsed Laser Deposition (PLD) in argon ambient atmosphere in the range of 10^{-5} Pa - 10 Pa. We performed a full characterization of the films by AFM, XRD, SEM, XPS and TEM, Hall measurements, photoluminescence, transmission and reflections spectroscopy and spectral ellipsometry. One of the most important parameters of p-type transparent semiconductor either in transistors and transparent conducting films or in sensors, are the electrical properties. Due to this we take advantages from our previous work and we carried out the in-situ resistance measurements during the PLD process as well as the monitoring of the resistance behavior after deposition, when the surface of the film came into contact with the surrounding atmosphere. To study the effect of the surface oxidation of CuI and CuBr film, the powerful technique near ambient pressure photoelectron spectroscopy (NAP-XPS) was carried out to investigation of surfaces composition in the presence of oxygen atmosphere. The idea was to observe the reaction of the surface of halides while exposed to atmosphere as a function of temperature as well as in-situ- resistivity measurements.

Keywords

copper halides, p-type, near ambient pressure XPS

O5.10

Friction properties of amphiphilic copolymers

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Abstract

The objective of this experimental work is to study the influence of the composition of amphiphilic copolymers containing a polar block (polyethylene glycol, PEG) and a non polar block (polyethylene, PE) on their friction properties. Different polyethylene-b-polyethylene glycol diblock copolymers (PE-b-PEG), with different PE/PEG ratios are used. Friction of copolymers spheres (4 mm diameter) is measured against two different substrates: a hydrophilic glass plate and a hydrophobic glass plate (grafted with a methyl-terminated silane). Friction tests are performed using a CSM pin-on-disk tribometer under ambient conditions, under a normal force equal to 1N and a friction speed of 1 mm/s. The friction coefficient, equal to the friction force divided by the normal force, is determined. The experimental results show a significant influence of the copolymer composition, with a surprising decrease of friction for higher PEG block content sliding against the hydrophilic substrates, explained by the effect of crystallinity degree of the PEG blocks. The influence of the nature of the substrate is also analyzed. Interfacial interactions between both blocks and the substrate surface play a major role, but both blocks being able to crystallize, the crystallinity of each block has also a significant effect on the friction behavior of copolymers.

Keywords

Friction, Amphiphilic copolymers, Surface energy, Crystallinity

O5.11

Impregnation methods for quantitative analyses of PEMFC MPL/GDL

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Abstract

Microstructural analysis is central to understand and predict the performance and degradation of proton exchange membrane fuel cell (PEMFC) materials. Advanced electron and x-ray 3-D microscopy methods are needed to characterize the reticulate structures forming the catalyst, gas diffusion layer/ microporous layers. The high-throughput dual beam scanning electron microscope allows the 3-D imaging of such layers with a spatial resolution in the range of a few nm. However, for accurate quantitative analyses, impregnation of the porous sample is required to mitigate artefacts due to milling and pore-through effect, and provide sufficient contrast between the material phases for image segmentation. This study investigates an impregnation method based upon the addition of Cobalt (II) acetylacetonate nanoparticles in an epoxy polymer resin. The results were compared with conventional methods using commercial resins stereology on sections polished by focused ion beam (FIB). The results indicate the appropriateness of the newly proposed method, providing adequate contrast for accurate image segmentation. An Energy Dispersive X-ray (EDX) analysis was included to obtain an information about the composition, which can be used for further improvements of the resin.

Keywords

Proton exchange membrane fuel cell, 3D electron microscopy, Cobalt (II) acetylacetonate, sample preparation and impregnation

O5.12

Ultrafast laser micro and nanoprocessing for biomedical applications

Xxx Sedao

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Abstract

In an ageing society, medical implants are more and more frequently used to replace certain human organs with deficiencies and/or failures in patient bodies. For the comfort and safety of the patient, it is vital to assure a good transplant integration, which implies a properly controlled cells adhesion and bacteria proliferation at the implant surface. Since vast varieties of microscale living life forms at the implant-body interface, including bacteria and cells, are known to be sensitive and reactive to the surface topography where they dwell, it is paramount to optimize the surface geometry of the implants towards a desired integration. For dental implants, for instance, this implies reduced bacteria settlement at the denture vicinity, enhanced sealing in the gum, and improved osteogenesis at the jaw. For other types of implant such as bone fracture fixtures and cardiac pacemakers, as they have to be removed in a fixed period of time, a reduced cells adhesion (such as scar tissue formation) is highly desirable. Ultrafast laser is a seemingly mighty tool for medical implant surface topography modification towards a controlled adhesion. In this communication, the laser patterning, and living micron-organisms' response to the laser texturization are discussed. Due to its biomedical application nature, it is equally of key importance to ensure laser patterning does not incur chemistry alteration at the implant surface. To this end, X-ray Diffraction spectroscopy (XRD), Scanning Transmission Electron Microscope (STEM) and Electron Energy Loss Spectroscopy (EELS) based analyses were deployed to investigate the surface after laser irradiation.

Keywords

ultrafast laser processing, implant, cell adhesion, hydrophobicity

05.13

Compositional and crystallinity spreads of $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ thin films deposited by chemical beam vapor deposition

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Abstract

Combinatorial methods have been successfully utilized for the rapid screening of novel functional materials in a multitude of research fields including catalysis and pharmaceutical discovery [1]. Here, we have used chemical beam vapor deposition (CBVD) to synthesize for the first time $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ thin films. CBVD technique relies on effusing molecular beams of chemical precursors emitted, in high vacuum conditions, from an array of punctual sources towards a heated substrate, on which the molecules decompose thermally [2]. The line-of-sight nature of the technique and the possibility to vary the number of active sources enable stoichiometric gradients over the deposition area. The amount of the precursors reaching a given position of the substrate can thus be finely controlled enabling stoichiometry tuning.

The obtained $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ thin films presented a wide range of stoichiometries, spanning from $\text{Na}_{0.4}\text{TaO}_{2.4}$ (i.e., $\text{Na}/\text{Ta}=0.4$) to $\text{Na}_{1.5}\text{TaO}_{3.4}$ (i.e., $\text{Na}/\text{Ta}=1.5$). The growth of an orthorhombic perovskite structure peculiar of NaTaO_3 was correlated to the composition and deposition temperature. Both high under-stoichiometries (e.g., $\text{Na}_{0.5}\text{TaO}_{2.5}$) and low experimental work temperatures (480 °C) resulted in an amorphous phase. The high deficiency of Na and O in $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ was the main reason behind the lack of perovskite formation at extreme under-stoichiometries. Conversely, both higher temperatures (550-620 °C) and moderate under-stoichiometries (e.g., $\text{Na}_{0.9}\text{TaO}_{3.0}$) led to a well-crystallized orthorhombic structure. High crystallinity was also observed at extreme over-stoichiometries (e.g., $\text{Na}_{1.5}\text{TaO}_{3.4}$), where the incorporation of additional Na in $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ occurred at inertial sites of the orthorhombic lattice [3].

The wide compositional and crystallinity spreads of $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ enabled by CBVD method are very promising for the fine-tuning of the functional properties of sodium tantalate-based thin films and their application in photocatalysis.

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Keywords

Chemical beam vapor deposition , Combinatorial investigation, $\text{Na}_{1+x}\text{TaO}_{3+\delta}$ thin films, Crystallinity spread

O5.14

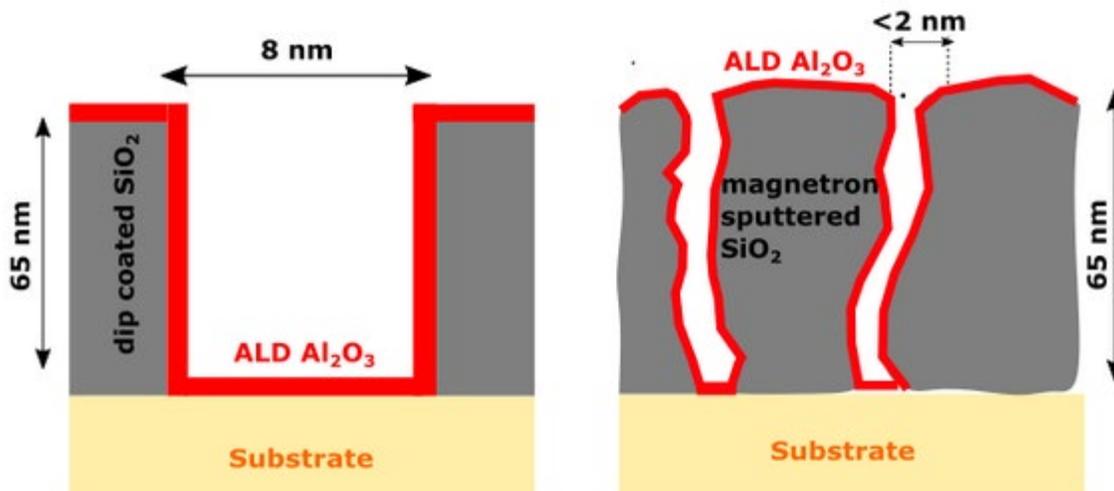
A comparison of precursor penetration depth of PE-ALD and thermal ALD of Al_2O_3 on microporous and mesoporous SiO_2

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Abstract

Recently Atomic Layer Deposition (ALD) has attracted much interest due to the possibility of tailoring thin-film membrane properties by the coating of internal pore walls thus altering both pore volume and chemistry [1]. Though Plasma Enhanced ALD (PE-ALD) has several advantages compared to thermal ALD, its usage in obtaining conformal coatings on high aspect ratio structures is limited due to the short life span of the reactive plasma radicals. The main objective of this work is to compare the precursor penetration depth and conformality of PE-ALD and thermal ALD layers of Al_2O_3 deposited utilizing the precursor trimethyl aluminium (TMA) on dip-coated mesoporous SiO_2 and magnetron sputtered microporous SiO_2 . These ALD coatings were analyzed using Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) to measure the AlO^+ fragment intensity at various depths of the sample. The ToF-SIMS measurements are supplemented by depth profiling X-ray Photo-electron Spectroscopy (XPS) measurements to measure the conversion efficiency of the adsorbed TMA into Al_2O_3 . The ToF-SIMS analysis of PE-ALD coatings indicate a non-conformal coating on microporous and mesoporous substrates. The ToF-SIMS analysis of thermal ALD coatings showed a strong dependence of conformality based on the porosity of the substrate.



Acknowledgements

This work was supported by the German Research Foundation (DFG) within the framework of the Transregional Collaborative Research Center TRR 87/1 (SFB-TR 87) "Pulsed high power plasmas for the synthesis of nanostructured functional layers".

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Keywords

PE-ALD, Thermal ALD, ToF-SIMS, Depth profiling XPS

O5.15

Density functional theory study of ethanol and formic acid adsorption on CaO(001)

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Abstract

Ethanol and formic acid adsorption on CaO (0 0 1) surface at low coverage is studied using Density Functional Theory (DFT) calculations with van der Waals corrections. We investigated the CaO surface in its rock salt structure. The more favorable sites for C₂H₅OH adsorption are on one (or two) Ca cations bonding the O atom from ethanol. H form (OH group) bond to surface oxygens with an adsorption energy of -1.12 (-1.14) eV. The distance of ethanol to surface is in the range of 2.3 - 2.5 Å . The molecule presents a strong elongation of the adsorbed O-H group being 53% (51%) larger than its molecular distance. Bond order analysis shows that distances and BO are similar for Ca-O molecule and Ca-O surface. A charge transfer occurs from O atom of the 2nd layer to Ca ions at 1st layer and the molecular O atom gain some charge, while H loses charge towards surface oxygen and from this to the rest of the surface. In the case of H-COOH we found two possible adsorption sites with -2.38 and -2.07 eV, again the O-H bond is elongated with respect to the molecular states. DOS and bonding analysis are performed in both cases.

Keywords

DFT, CaO, ethanol, formic acid

O5.16

Tribochemical study of Ni₆₂Nb₃₃Zr₅ metallic glass depending on the Cr content of steel counterparts

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Abstract

Bulk Metallic Glasses (BMG) are known to demonstrate exceptional mechanical properties combining very high yield stress and fracture toughness with large elastic strain limit. There is, however, no consensus regarding the suitability of BMG for tribological applications, because literature reports conflicting behavior in friction. Nonetheless two recent studies conducted respectively at the nanoscale [1] and at the macroscale [2] are suggesting that it is possible to control friction and wear of BMG by carefully selecting the counterpart based on its elemental composition. The present study demonstrates the control of the friction of Ni₆₂Nb₃₃Zr₅ BMG by adjusting the Cr content of the steel ball counterpart. Three different steels with similar C content, but different Cr contents were chosen as sliding counterparts.

Highly repeatable friction behavior with friction coefficient varying from 0.1 to 0.9 depending on the steel was observed. In all cases, samples exhibited extremely low wear making it impossible to be measured quantitatively. To elucidate the mechanism driving such tribological behavior, the interfacial material created during friction has been analyzed by SEM/EDS, Raman spectroscopy, XPS, and NanoSIMS which has shown a strong affinity of Cr, Fe, and Ni, all 3 located in the same regions. Nb and Zr tend to be detected together in a different location. Distribution of O over the different regions and subsequent in-depth analysis of the NanoSIMS mass spectra showed that CrFe₂O₄, Fe₃O₄, NiFe₂O₄, are most likely created in Ni and Fe rich regions. Their relative proportion depending on Cr content of the steel ball is believed to be responsible for the varying level of friction coefficient.

[1] A. Caron, *et al.*, ACS Appl. Mater. Interfaces 5 (2013) 11341.

[2] P.-H. Cornuault, *et al.*, Tribol. Int. 141 (2020) 105957.

Keywords

Tribology, Tribochemistry, Bulk Metallic Glass, NanoSIMS

O5.17

Investigation of surfactant-membrane interaction using molecular dynamics simulation with umbrella sampling

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Abstract

Membranes are effective for removing oil emulsions in oily wastewater treatments, which is important for environmental remediation as well as recovery of oil for economic benefits. Surfactants play a critical role in stabilizing the oil emulsions, but their effects on the inevitable membrane fouling phenomena remain poorly understood. The focus here is the interesting flux enhancement relative to water conferred by the cationic cetyltrimethylammonium bromide (CTAB) surfactant. Molecular dynamics simulations were performed to understand the interactions between three different surfactants and a hydrophilic polyvinylidene fluoride (PVDF) surface. Unbiased MD simulations quantify the surfactant–water, surfactant–membrane, and water–membrane interactions, but none appears well-correlated to the relative flux trends due to the interplay of all three interactions. To account for all interactions concurrently, umbrella sampling was performed to obtain the potential of mean force (PMF) curves. The adsorption of all three surfactants is driven by enthalpy (rather than entropy), and CTAB was found to have the most attractive binding free energy, smallest equilibrium distance, and looser water network near the PVDF surface, which are tied to the experimental observation of flux enhancement and highest retention. The Angstrom-scale results here reveal the need to consider all the interactions simultaneously rather than separately to fully account for mechanisms underlying membrane fouling by surfactants.

DOI: <https://doi.org/10.1021/acsestengg.1c00262>

Keywords

Surfactant, Membrane filtration, Flux enhancement, Molecular dynamics simulation

O5.18

Evaluation of the effect of post-plasma reactions in water on the work function of graphene paper

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Abstract

Plasma functionalization is increasingly used to endow carbon materials with surface functionalities, especially with various oxygen groups. To evaluate electron donor properties of graphenic surfaces work function is often used as a descriptor for optimization of new series of materials. However, the actual application of materials may be some time after the modification was performed, and what is more, in a different environment, e.g. in an aqueous solution. The presented research addresses the problem of instability of plasma-induced changes of carbon materials. This problem, although neglected for many years, has drawn attention in recent time, and the loss of surface activity was pointed out. In our study we evaluated the maximum work function changes which can be achieved by using various oxidative plasma treatments and the speciation of the resulting oxygen groups before and after immersion of the plasma-treated samples in water. We used pure oxygen, air, 5% O₂ in He, CO₂, and Ar as feed gasses for plasma generation. The critical plasma parameter (plasma power, total pressure, modification time) for each gas composition was evaluated to achieve maximum work function changes using a design of experiments approach, and then further optimization was performed. We found that functionalization degree and electronic properties of the plasma-modified graphene paper highly depend on the post-plasmatic reactions in water, which increase the concentration of surface oxygen groups. Similar maximum of the work function changes after immersion in water are obtained for oxygen and air plasmas, albeit for different total pressure in plasma chamber and different treatment time. In the case of air plasma, the changes are brought about by the introduction of high amount of surface oxygen species, with high fraction of COO groups, while for pure oxygen plasma there is a lower overall oxygen content with the C-O groups as dominating surface groups.

Keywords

carbon, electronic properties, plasma functionalization, oxygen functional groups

O5.19

Functionalization of fluoropolymers using atmospheric pressure dielectric discharges

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Abstract

Today, fluoropolymers are widely employed in different industries, including textiles, buildings, and medical instruments. Their chemical inertness and low friction coefficient make them suitable for different applications. However, their low surface energy leads to poor adhesion during the assembly of composite devices. Among the different techniques used to enhance their adhesion, atmospheric pressure discharges provide a fast and low-cost method with a reduced environmental impact. The highly energetic species present in the ionized gas allow the breaking of molecular bonds in the gas phase and the growth of thin films on the polymer surface. Although this approach has proven to be efficient, the different chemical and physical processes happening in the discharge remain not fully understood. In this study, we modified fluoropolymer surfaces by atmospheric pressure dielectric barrier discharge using nitrogen and an organic precursor. Infrared spectroscopy in the attenuated total reflectance mode (ATR-FTIR) was used to evaluate the modifications on the first top micrometers of the samples. The effect of the experimental conditions used to sustain the discharge on the precursor fragmentation was studied by curve fitting the peaks in the 1500 - 1800 cm⁻¹ range. The results show the formation of a variety of new hydrophilic functionalities and several experiments are performed to build a better fundamental understanding of the mechanism of formation of these bonds at the fluoropolymer surface. Finally, profilometry was used to correlate the plasma parameters to the growth rate of the different thin films produced. These promising results represent a significant step toward a deeper understanding of the chemical modifications induced on fluoropolymers by this dry process.

Keywords

Fluoropolymer, Organic precursor, Plasma atmospheric pressure, Growth mode

O5.20

Oxygen absorption in amorphous and nanocrystalline HfNbTaTiZr high-entropy alloy thin films

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Abstract

Refractory high entropy alloys (HEAs) represent an attractive candidate for novel hydrogen storage materials. Their superior hydrogen sorption capacity originates from large lattice distortion. Structure refinement down to nanoscale or eventually amorphization of the alloy may further improve hydrogen absorption properties. Nevertheless, the effective suppression of the oxidation of refractory HEAs at ambient atmosphere is essential.

In this study, various HfNbTaTiZr thin films (thicknesses from 100 nm to 300 nm) with amorphous to nanocrystalline microstructures were fabricated by DC magnetron sputtering. The deposition temperature was found to be a crucial parameter, deciding whether the growing film will be amorphous or crystalline. At room temperature, a sluggish diffusion of deposited atoms does not allow to form nucleates of a coherent phases, which results in an amorphous film. At the elevated temperatures of 600 C and 700 C, it was observed the formation of three non-HEA phases: HfZr-rich hcp phase, NbTa-rich bcc phase, and balanced bcc2 phase. Positron annihilation spectroscopy using a monoenergetic slow positron beam is an excellent technique with a high sensitivity to vacancy-like open volumes present in thin films. Amorphous structure exhibits a high density of defects of a size comparable with monovacancies to large vacancy clusters. *In-situ* annealing of the as-deposited amorphous film at 600 C and 700 C for 1 hr leads to crystallization of the film, while the open structure is preserved. Therefore, we are able to tune the crystalline structure as well as the defect structure of the deposited films.

Oxygen absorption in HfNbTaTiZr films at the ambient atmosphere was investigated by X-ray photoelectron spectroscopy combined with depth profiling. An open structure of amorphous films causes excessive oxidation of the film compared to the more compact nanocrystalline films, where the oxide is formed only at the surface.

Keywords

high-entropy alloys, thin films, positron annihilation spectroscopy, x-ray photoelectron spectroscopy

O5.21

Adsorption of PAH derivatives on metals: Properties and reactivity upon external stimulation

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Abstract

Over the two past decades, on-surface covalent synthesis of organic nanostructures has been widely investigated in the aim of fabrication of molecular electronic components and functional nanomaterials. Depending on the adequation between the functional groups available on the organic compounds, the symmetry of the molecule, the reactivity and symmetry of the hosting surface, it is possible to drive different on-surface reactions and favors the formation of new organic architectures of a specific shapes and properties. [1,2]

Among the different possible organic compounds available polycyclic aromatic molecules such as polycyclic aromatic hydrocarbons (PAHs) and their derivatives are widely investigated because of their particularly interesting potential spanning from astrochemistry to nanotechnology or spintronics. [3,4]

In this framework, we report the study of the PAH derivatives molecules, such like dibenzophenazine (DBPA), adsorbed on metals. Using a unique combination of several surface-sensitive techniques from high-resolution electron energy loss spectroscopy to photoemission spectroscopy and scanning tunneling microscopy together with optical techniques, we probed the physical and chemical properties of highly ordered films of DBPA molecules adsorbed on low-index metallic surfaces, together with their reactivity. More particularly we discuss their evolution under UV irradiation and thermal annealing, reporting the formation of new chemical bonds reflecting the evolution of this system upon external stimulation.

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Keywords

on-surface chemistry, photoreaction, spectroscopy

O5.22

HyStor: Development of novel silica barrier coatings for mitigating H₂ permeation: I – preliminary barriering effect of mesoporous oxide structure

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Abstract

With the emerging focus of Hydrogen as a fuel in the Green Economy, there is an urgent need to deliver solutions related to the safe and efficient storage and transmission of Hydrogen. Two critical areas related to both cost efficiency and safety relate to the highly permeable and corrosive properties of Hydrogen molecules as a gas. One area of focus is the formation of barrier coatings to limit both hydrogen permeation as well as reducing its corrosive effects upon the underlying substrate of the storage vessel material. While the formation of barrier coatings as part of the production process of the storage vessels and piping is the primary goal, a secondary goal is to apply such protective coatings in situ within existing infrastructure, such as storage vessels and pipes.

This project will focus on the synthesis and application of novel sol-gel coating materials based on Silica as a flexible approach to deposit barrier layers as a multilayer coating in a cost-effective way.

As part of this approach, the process of sol-gel maturation and understanding the forces that drive silica network development and interaction between hydrogen and the newly-developed coated surface will be studied dynamically using a range of surface-measurement instruments.

This presentation highlights the limitation of H₂ permeability through polymer membrane by a silica sol-gel coating at 2 bar of hydrogen overpressure and its correlation with unhydrolysable organic moieties in the oxide structure.

The research was supported by the National Center for Research and Development in Poland under the Small Grant Scheme (SGS) project 'Improving the Efficiency of Hydrogen Storage Vessels through Novel Oxide Coatings HyStor NOR/SGS/HyStor/0306/2020-00' Programme 'Applied Research' financed through the Norwegian Financial Mechanism

Keywords

barrier coating for hydrogen, silica structure, sol-gel technology, low pressure permeation

O6.01

Hybrid cellulose-QDs composites – from synthesis and characterization to application

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Abstract

Nowadays, there is a relentless search for new types of materials, especially those that could improve the conventional materials already in use. Various composites or hybrid materials provide a good answer to those demands. The use of cellulose, one of the most abundant natural polymers is still rare due to its insolubility in water and most organic solvents, hygroscopic nature, and other properties such as poor wettability, moisture absorption, etc. Looking at the field of semiconductors, such as various optical devices, photonics, fluorescent probes, etc., preparing cellulose-based composites could facilitate surpassing the abovementioned limitations. For example, blending can be done with fluorescent semiconductive material, namely CdSe quantum dots (QDs). Combining QDs with cellulose matrix should lead to stabilized QDs, and improve and highlight their functionality in general. Our goal is to develop a method for preparing well-defined hybrid nano- or microcellulose-QD composites with tunable optical properties. Synthetic procedures depend on the species of QD capping ligands and temperature in particular, as the key parameters for dynamics control.

In this work, a comparison of nano and micro cellulose-QDs composites is presented. Prepared CdSe-cellulose composites are further characterized by UV-VIS, SEM, XRD, and contact angle measurements. XRD confirms composition with broad amorphous cellulose signal, while several wide diffraction lines are attributed to CdSe QDs. Moreover, microscopy and surface energy by CA measurements provided insight into the connectivity and miscibility of QDs and cellulose. Obtained results enable improvements in the course of the QDs preparation. The main goal is to gain control over the synthesis procedures necessary to produce this composite in a thin-film configuration, which is suitable for charge transfer layer application in solar cells and will be tested by Impedance spectroscopy.

Keywords

quantum dots, cellulose, composites, impedance spectroscopy

O6.02

Synthesis and characterization of designed electrospun zirconia nanofibers in different annealing temperatures

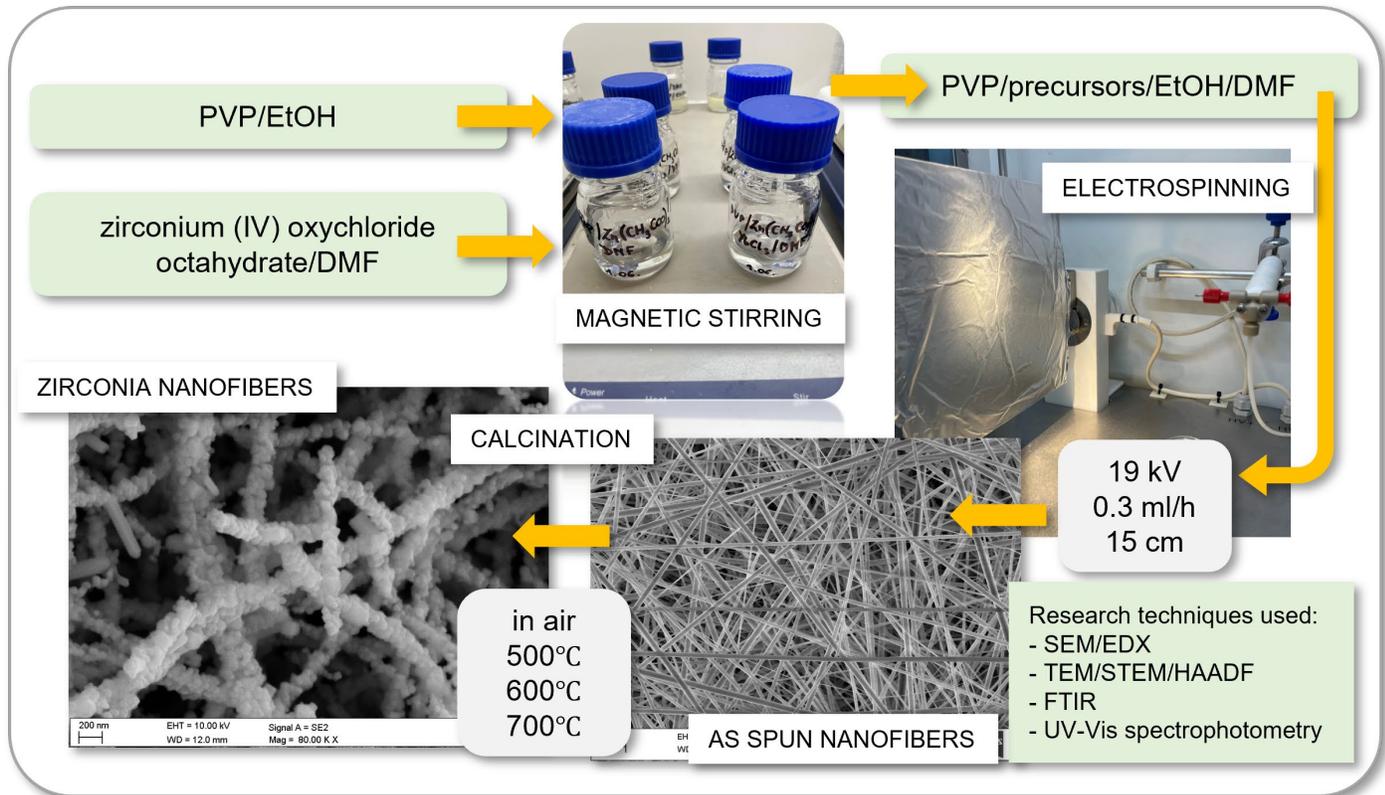
Tomasz Tanski, Marta Zaborowska, Weronika Smok

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Abstract

The aim of this paper was to manufacture highly crystalline zirconium oxide nanofibers using zirconium (IV) oxychloride octahydrate as a ZrO_2 precursor. The preparation procedure was as follows: 10% wt. solution of polyvinylpyrrolidone in ethanol was mixed with zirconia precursor in DMF solution. In the next step, electrospinning process of polymer-ceramic nanofibers manufacturing was conducted, using parameters such as solution flow rate of 0,3 ml/h, the potential of the electrodes of 19 kV and the distance between the syringe and the flat collector of 15 cm at horizontal electrospinning set up. High-temperature thermal treatment was evaluated for three different temperatures and the influence of different annealing temperatures on morphology, crystallinity and optical properties, including transmittance, absorbance and width of energy band gap was analysed. Moreover, SEM/EDX, TEM (HAADF) and FTIR advanced techniques were used to examine the morphology and structure of fabricated ceramic nanofibers.

Zirconium oxide (ZrO_2) is one of the most commonly used metal oxides, among others in catalysis, filtration, gas sensors and solid oxide fuel cells. Applying different annealing temperatures of polymer-zirconia precursors nanofibers results in variety of allotropic modifications; low-temperature monoclinic and high-temperature tetragonal and cubic. Functional one-dimensional nanostructures possess large potential applications, based on their properties which are dependent on fibers morphology, diameters, porosity, chemical composition and specific surface area. Moreover, optical and electrical properties can be adjusted by various polymer and precursor concentration and/or dopants in spinning solutions and different morphologies can be obtained. Thus, it is crucial to optimize fabrication parameters in order to produce nanostructures with desired functionality. Electrospinning process is a versatile method of producing one-dimensional nanomaterials of which eligible properties of final products can be achieved.



Keywords

electrospinning, nanofibers , optical properties, structure

O6.03

Hybrid metal-containing plasmonic nanostructures based on Si and Ag

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Abstract

The combination of nanoplasmonics and well-developed semiconductor technology is one of the current trends. This combination will make it possible to create functional hybrid nanostructures for various sensors and optoelectronic devices embedded in a chip. Monocrystalline Si was selected as a semiconductor material and Ag nanoparticles (AgNPs) were selected as a plasmonic material. On their basis, two types of hybrid nanostructures have been proposed. The morphology of all these structures was investigated by Atomic Force and Scanning Electron Microscopy (SEM) and the optical properties were obtained by Spectroscopic Ellipsometry and Photometry (SP).

1. "Metal-semiconductor". AgNPs were obtained on a Si substrate by reduction from an AgNO₃+HF solution with different reagent ratios (Fig.1a). The morphology of AgNPs was modified by annealing at 350°C to obtain hemispherical NPs of various radii (Fig.1b-e). A shift of the localized plasmon resonance to the near-IR range due to an increase in the radius of AgNPs was found. The regions of disordered hemispherical AgNPs selected from SEM images and the distribution of the electromagnetic field in the structures were calculated in COMSOL Multiphysics by translating finite regions. The calculated reflection spectra of hemispherical AgNPs for p- and s-polarized light are in good agreement with the experimental data obtained by SP (Fig.2).

2. "Dielectric-metal-semiconductor". Pyramidal AgNPs were obtained due to the anisotropy of Si oxidation upon annealing at 1000°C, coated with a layer of thermal SiO₂ (Fig.3a-f). The dependence of the position of the localized plasmon resonance as a function of the SiO₂ thickness has been established; a strong localization of the electromagnetic field ("hot spots") was found near the corners of pyramidal AgNPs embedded in the Si substrate. The AgNPs structures coated with a SiO₂ layer are stable and inert to external influences. All structures of two types are promising for use as surface-enhanced Raman scattering substrates.

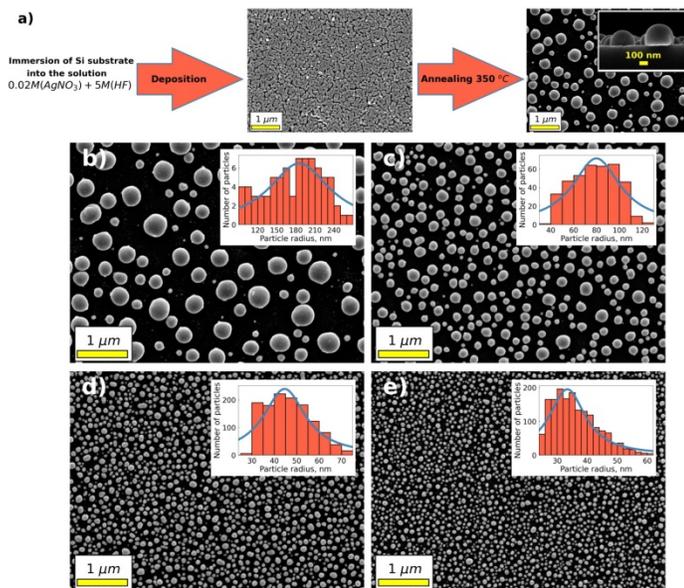


Fig. 1 (a) Process diagram and SEM images of morphological changes after Ag deposition (30 sec) and annealing at $350\text{ }^\circ\text{C}$ (30 min) in air; p-type Si with $\rho = 10\text{ Ohm}\cdot\text{cm}$ and crystallographic orientation (100) are used as substrates; SEM images (top view) of AgNPs after annealing and Gaussian particle size distribution for the corresponding $AgNO_3 + HF$ solution ratios: (b) 1:1, (c) 1:4, (d) 1:6 and (e) 1:8.

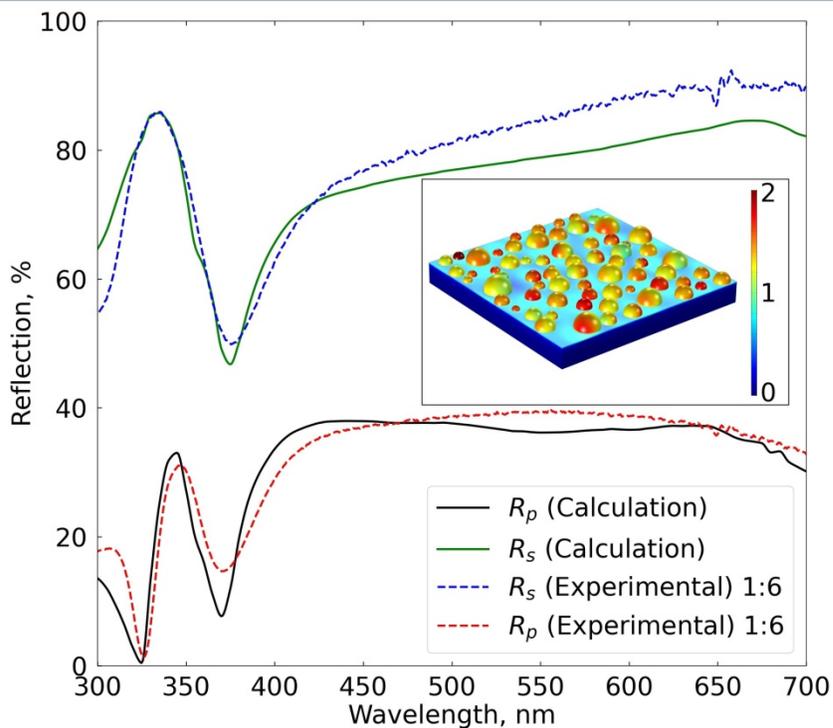


Fig. 2 Experimental (dotted line) and numerical (solid line) reflectance spectra for p- and s-polarized light from annealed AgNPs in the ratio (1: 6); (in the insert) numerical model ($1\text{ }\mu\text{m} \cdot 1\text{ }\mu\text{m}$) obtained from the SEM image of annealed AgNPs in the ratio (1: 6) and the distribution of the electric field modulus for p-polarized light at a wavelength of 324 nm corresponding to the bulk plasmon resonance.

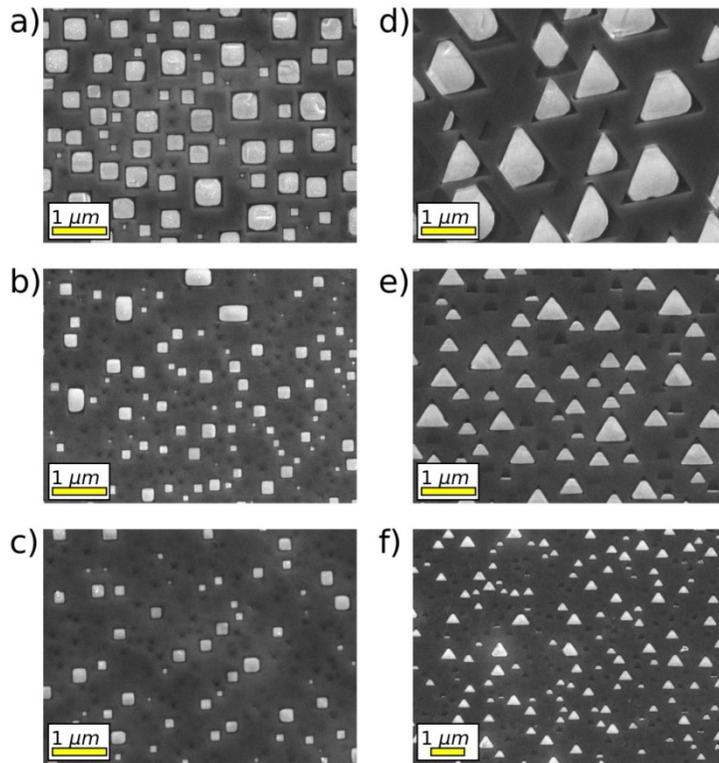


Fig. 3 SEM images (top view) of embedded AgNPs (without SiO₂ layer) after annealing at 1000 °C in water vapor for the corresponding solution ratios and crystallographic orientation of Si: (a) 1:1 (100); (b) 1:5 (100); (c) 1:10 (100); (d) 1:1 (111); (e) 1:5 (111) and (f) 1:10 (111).

Keywords

Localized plasmon resonance, Si and Ag, Annealing, COMSOL Multiphysics

O6.04

Electronic properties of the interfaces between Cu-phthalocyanine and 2H-MoS₂ and 2H-TaS₂ single crystals

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Abstract

Transition metal dichalcogenides (TMDs) and their interfaces with organic semiconducting molecules have drawn much interest in the scientific community due to possible applications in organic electronics. Knowledge of the electronic properties of such interfaces are key in understanding and often optimizing the device performance. In the present work, X-ray and Ultraviolet photoelectron spectroscopies (XPS and UPS) were utilized to study the effect of the transition metal of the dichalcogenide with the interfaces they form with Cu-phthalocyanine (CuPc). The interfaces were formed by in-situ gradual thermal evaporation of the CuPc molecule onto the basal plane of 2H-MoS₂ and 2H-TaS₂. The 2H polymorphs of the MoS₂ and TaS₂ were utilized as substrates, since MoS₂ is a semiconductor with an energy gap of about 1.3 eV, while the valence band edge of the TaS₂ is dominated by the Ta 5d orbitals, giving it a metallic character. A phthalocyanine molecule was selected for this study as this family molecules often possess excellent electronic properties and are commonly utilized in microelectronic devices research. The experimental results show that from the early stages of the interface formation, a charge transfer occurs between the CuPc and the TMDs. The CuPc was found to orient parallel to both surfaces up to the first monolayer, while for the subsequent layers, it gradually tilts to assume a perpendicular orientation. From the energy diagram of the CuPc/MoS₂ interface, a hole barrier of 0.3 eV and an electron barrier of 0.8 eV are derived, favouring electron transfer from the CuPc to the MoS₂, while in the case of the CuPc/2H-TaS₂ interface, a Schottky barrier of 0.8 eV is formed.

Keywords

phthalocyanine, XPS, UPS, Transition metal dichalcogenides

O6.05

Preparation of anthraquinone-bridged g-C₃N₄/NiTiO₃ Z-scheme-based composite for efficient photocatalytic H₂ generation

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Abstract

The photocatalytic efficiency of Z-scheme-based photocatalytic systems is determined by the transfer rate of photo-generated charge carriers. Here, a novel indirect Z-scheme-based photocatalytic system was prepared by introducing anthraquinone (AQ) between g-C₃N₄ and NiTiO₃ by a hydrothermal method. Spectroscopic characterization data reveal that the anthraquinone is bridged between g-C₃N₄ and NiTiO₃, which allows the transfer of electrons through a conductive channel, suppressing the recombination rate of photogenerated charge carriers. An amount optimized of AQ in the g-C₃N₄/NiTiO₃ composite exhibits the excellent photocatalytic activity for the hydrogen production, which is twice that of the g-C₃N₄/NiTiO₃ composite under visible light irradiation. The significantly enhanced photocatalytic activity is attributed to the reversible redox reaction of AQ, which facilitates the recombination of conduction band electrons of NiTiO₃ with valence band holes of g-C₃N₄. The Z-scheme charge transfer mechanism of the AQ-bridged g-C₃N₄/NiTiO₃ composite is corroborated by the radical trapping experiments. A plausible photocatalytic hydrogen production mechanism is proposed. The current study opens a new avenue for the development of Z-scheme-based photocatalytic materials via the introduction of an AQ bridge in the existing composite materials to further improve the charge separation efficiency.

Keywords

g-C₃N₄-AQ-NiTiO₃, Z-scheme based photocatalysts, hydrogen production, anthraquinone bridge

O6.06

Selectivity in atomically precise deposition and etching

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Abstract

This presentation will cover recent advances in atomically-precise surface processing utilizing atomic layer deposition and atomic layer etching. The main focus will be on highly selective and efficient chemical methods for complex alloys such as CoFeB. This material is used to form a central unit in an integrated memory device, a magnetic tunnel junction (MTJ) consisting of two ferromagnetic layers, often using complex alloys such as CoFeB, separated by an insulating barrier such as MgO. At the nanoscale, it is imperative to maintain the concentration of each element in an alloy during etching, and it is important to not affect the insulating barrier, i.e. the etching process should stop at MgO. Here we use thermal dry etching of CoFeB alloy thin films with sequential doses of chlorine and 2,4-pentanedione (acetylacetone, acacH). Patterned samples are modified with atomic level precision, and the process is completely selective to the removal of CoFeB alloy in ALE regime without changing the alloy composition and without etching MgO that is used as a protecting layer. The second part of the presentation will highlight the new approaches to form a monoatomic resist layers based on halogenated silicon surfaces to suppress the atomic layer deposition of TiO_2 from TiCl_4 and water. The role of defects in deposition processes will be compared for differently functionalized silicon.

Keywords

Atomic layer deposition, Atomic layer etching, metal alloys

O6.07

Probing the correlation between the morphology and the optical anisotropy of ZnTPP films

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Abstract

Vacuum-deposited films of tetraphenylporphyrins (TPP) have been recently investigated for their ability in protecting the electrode surfaces from corrosion and damaging effects due to the environment. The protective action of porphyrin films is strongly related to both the molecule-substrate and molecule-molecule interactions, which determine the type of film growth (*e. g.*, layer-by-layer or layer-plus-islands) and its morphology. An exemplary case is offered by meso-tetraphenyl porphyrin-Zn(II) (ZnTPP), which shows different types of molecular aggregation, depending on the substrate or on the deposition and post-growth procedures. Finding the best strategy to reach a well-defined target for the film morphology plays a key role for the realization of effective protective coatings for electrodes.

Within this context, we present the investigation of the morphological variation of thin ZnTPP films, as a function of the substrate temperature, ranging from -200 °C to +200 °C. ZnTPP molecules were sublimated by an organic molecular beam epitaxy (OMBE) system onto a highly oriented pyrolytic graphite (HOPG) substrate, controlled in temperature by using a variable temperature cryostat. The film morphology and type of growth were characterized *ex situ* by both atomic force microscopy (AFM) and reflectance anisotropy spectroscopy (RAS), the latter being highly sensitive to the orientation and type of aggregation of the ZnTPP molecules on the substrate.

These results will help us to select the more promising molecular coverages for the electrode surface, whose effectiveness will be checked in the future, by performing suitable corrosion tests.

Keywords

porphyrin, optical anisotropy, reflectance spectroscopy, protective coating

O6.09

Investigation of the optical transitions in two-dimensional semiconductors by spectroscopic ellipsometry and first-principles calculations

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Abstract

Atomically thin semiconductors, e.g., the transition metal dichalcogenides (TMDCs), have appealed lots of attentions due to their specific features. Understanding the physical essential in optical properties of 2D semiconductors can guide the design and enhance performance of related photoelectric devices. Here, we propose a method to systematically determine and reveal the optical transitions in semiconductors by combining the spectroscopic ellipsometry, critical point (CP) analysis and first-principles calculations. The single crystal monolayer WS_2 is taken as an example to demonstrate the proposed method. Figure 1 shows the experimental and G_0W_0 -BSE calculated dielectric functions of monolayer WS_2 , indicating the excellent match between theoretical and experimental results. Then, we precisely determine the center energies of optical transition CPs A–F by CP analysis, as illustrated in Figure 2(d). By comparing the center energies of these CPs with energy difference between valence and conduction band pairs, as showed in Figure 2(c), we can determine the optical transition positions in band structure and partial density of states (PDOS). Figure 2(a, b) show that the optical transitions at CPs A–F are related to different electron transitions from first three valence bands to first two conduction bands, and these transitions are caused by the $W-5d$ and $S-3p$ orbitals.

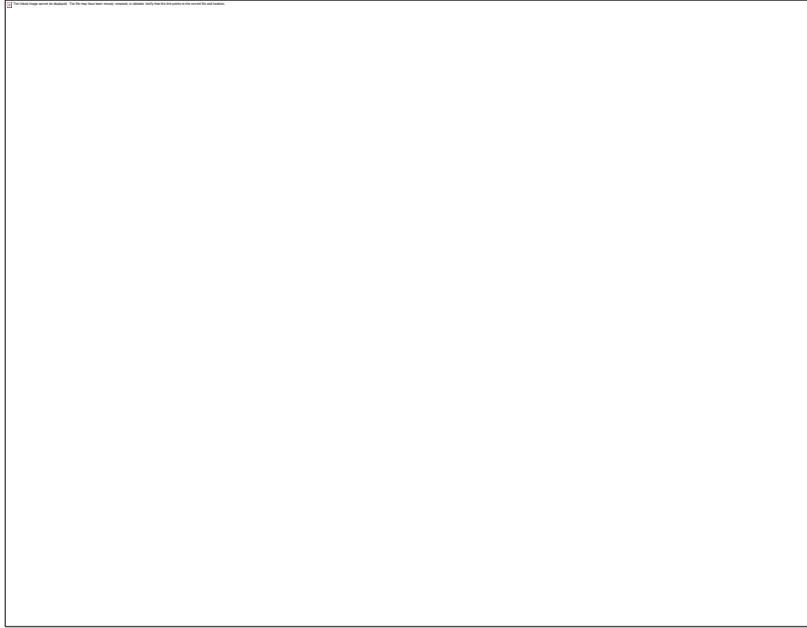


Figure 1. (a, b) Dielectric functions of single crystal monolayer WS₂. The inset shows the measurement process taken by a charge coupled device (CCD) camera (c, d) Dielectric function of monolayer WS₂ calculated by G₀W₀-BSE method.

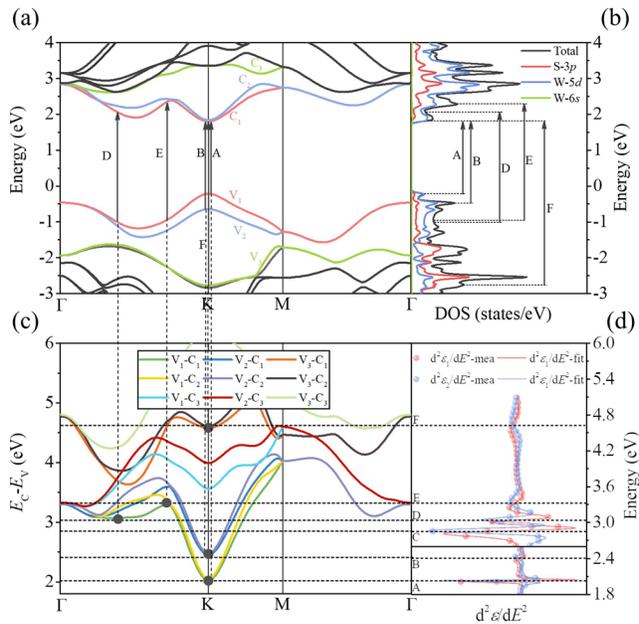


Figure 2. (a) Band structure of monolayer WS₂. (b) Partial Density of States (PDOS) of the monolayer WS₂. The labels A–F in (a) and (b) tag the inter-band transitions corresponding to relevant Critical Point (CP). (c) Energy difference between valence and conduction band pairs. (d) Second derivative of the dielectric function of monolayer WS₂.

Keywords

optical transition, 2D semiconductor, spectroscopic ellipsometry, first-principles calculations

O6.10

Characterization of the peculiar magnetic behaviour of ultra-thin Fe/Ni multilayers grown on the oxygen-reconstructed Fe(001) surface by spin resolved photoemission spectroscopies

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Abstract

The growth of epitaxial Fe/Ni heterostructures offers the unique possibility of stabilizing unusual crystallographic phases, possibly characterized by novel electronic and magnetic properties [1].

We present a structural and spectroscopic characterization of Ni and Fe multilayers grown on *bcc* Fe. At variance with previous literature investigations, the substrate is treated in order to form an oxygen superstructure, namely the Fe-*p*(1x1)O surface. The presence of an oxygen overlayer, capable of floating at the Ni/Fe sample surface even at room temperature, contributes to a peculiar morphological evolution and intervenes in the structural relaxation of the metastable Ni overlayer, as anticipated by our previous studies [2].

In the present work, we extend our investigation on the magnetic properties of the multilayer, at each step of the growth, by the combined use of *in-situ* spin-resolved photoemission spectroscopy (SR-PES) and inverse photoemission spectroscopy (SR-IPES). A strong decrease of the spin polarization is observed at the surface as the thickness of the *bcc* Ni layer increases, with a clear quenching of the magnetization. When iron is deposited on 6 ML Ni on Fe-*p*(1x1)O, there is an abrupt restoration of the spin polarization, even at one monolayer coverage, as also obtained from density functional theory (DFT) calculations. Moreover, we observe the disappearance of a feature related to majority electrons above the Fermi level, directly linked to the presence of the underlying buffer layer. The abrupt restoration of the Fe magnetization combined with the changes observed in the electronic structure above the Fermi level are the evidence of the peculiar magnetic properties of this multi-layered system.

[1] Lennart, Soroka and Kamali, J. Phys. Conf. Ser. 217 (2010) 012112

[2] Picone, Bussetti, Riva *et al.*, Phys Rev B 86 (2012) 075465

Keywords

magnetic materials, ultra-thin multilayers, Spin-resolved photoemission, spintronics

O6.11

Alternative dry process to treat fluoropolymers and enhance their adhesion by atmospheric pressure plasma

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Abstract

Fluoropolymers (FPs) stand out among other polymers due to their chemical inertness, temperature stability, low coefficient of friction, dielectric properties, and low surface energy. They are employed in numerous sectors, including automotive, textile, electronics, coatings, and biomedical industries. However, a surface modification is often required to increase their adhesion and compatibility with specific targets (*e.g.*, adhesives, cells). Therefore, wet-chemical treatments have been extensively used to modify their surface. Nevertheless, these treatments employ hazardous reagents and environmental regulations are applied due to the harmful residual products involved. Plasma surface modification stands as dry process capable of producing surface modifications with low consumption of chemical products. This approach can enhance properties such as adhesion, wettability, and biocompatibility without affecting the polymer bulk properties. However, the fine-tuning of surface properties by using plasma processes at atmospheric pressure remains a challenge to be solved. Accordingly, better understanding of FPs modifications by this process will provide an eco-friendly alternative to other chemical methods.

In this work, the relation between the experimental parameters used to sustain the plasma discharge and the surface properties have been studied to increase the adhesion properties of FPs. Our results suggest that, by pulsing the electrical signal (duty cycle) and controlling the residence time of the polymer inside the discharge, it is possible to tune the surface modifications. This affects the defluorination rate, the wettability, and the surface energy of the polymers. More specifically, X-ray photoelectron spectroscopy highlights that increasing the dose leads to an increase in C/F ratio on the surface. Also, this allows nitrogen and oxygen-containing functionalities to be embedded in the FPs surface. The adhesion was evaluated by T-peel test with silicones, acrylics, and rubber adhesives. The results indicate that the adhesive response depends on the adhesive used. The highest peel strength has been observed with acrylics and rubber adhesives.

Keywords

Fluoropolymers, Adhesion, Atmospheric pressure plasma, Peel test

O6.12

On the pulsed laser deposition of copper halides thin films: controlling the optical and electrical properties by in situ plasma diagnostics

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Abstract

This work reports the production of high-quality copper halide thin films deposited in various Ar pressure (10^{-5} Pa - 10 Pa) range at room temperature. Resistivity measurements, charge mobility and carrier concentration were estimated to have a full characterization for these p-type semiconductors. To receive complex information about the films properties, the fabricated films were characterized by XRD, AFM, SEM, XRF, XPS, Hall measurements, photoluminescence, transmission and reflections spectroscopy and ellipsometry. The attention was focused on the effect of angular distribution of the plasma properties on the spatial resolution homogeneity of the properties of the films. The Cu vacancies play a significant role in the p-type conductivity of CuI and CuBr films. Due to this, the attention will be focused on the study of the Cu or halide vacancies. To identify phenomena behind the formation of defects in detail we used: photoluminescence measurements, thermal stimulated luminescence, Electron Paramagnetic Resonance and positron annihilation spectroscopy. The surface analysis investigation revealed a congruent transfer from the target coupled with a good crystallinity of the films and good electrical properties. In order to understand the deposition process of Cu halides we implemented Langmuir probe technique and Optical Emission Spectroscopy for angular, space and time-resolved measurements. The halide plasmas present some complex features of the ionic cloud as seen by unbiased probe analysis as a time-of-flight measurement tool. Each feature corresponds to an ionization state of the Cu and halide ions, results confirmed by spectroscopic investigations performed along the main propagation axis and discussed in the framework of multiple double layer formation during plasma expansion. The nature and pressure of each used gas influenced the emission in a unique manner, which was well correlated with the data collected by the electrical measurements.

Keywords

pulsed laser deposition, halide thin films, in situ plasma monitoring, Langmuir Probe

O6.13

Spin-polarized photoemission from chiral CuO catalyst surfaces

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Abstract

It was recently demonstrated that chiral cupric oxide (CuO) layers can spin-polarize (photo)electron currents, and this capability was linked to the occurrence of the chirality-induced spin selectivity (CISS) effect in these layers¹. While the CISS effect is established in organic chiral molecules, its emergence in chiral but inorganic, non-molecular materials is not yet fully understood. Here, we provide further insights into the underlying mechanism. Chiral CuO films were electrochemically deposited on partially UV-transparent polycrystalline gold substrates. Photoelectrons were generated with laser pulses at 213 nm, and their average spin polarization was measured in a Mott scattering apparatus. By changing the direction of illumination and energy resolving the photoelectrons, the relative numbers of photoelectrons originating from the substrate versus those from the oxide layer were distinguished. The findings reveal that the spin polarization is strongly energy dependent and that the measured polarization values can be rationalized as a sum of an intrinsic spin polarization in the chiral layer and a spin-filtering contribution.

¹ K.B. Ghosh et al., J. Phys. Chem. C 123, 3024-3031 (2019)

Keywords

chirality-induced spin selectivity, electron spin, cupric oxide, photoemission

O6.14

Synthesis of mesoporous hafnium oxide nanocrystals by precipitation method for detection of ethanol gas with high sensitivity

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Abstract

The synthesis of nanostructured metal-oxides with a highly porous nature to efficiently detect ethanol gas is an essential issue in gas sensor technology. In addition, the development of a facile synthesis method is required to yield a considerable amount of nanopowders for technological applications. Herein, an alternative ethanol chemosensor based on the hafnium oxide (HfO₂) nanoparticles is proposed, operating at room temperature with enhanced sensitivity and stability. Large yields of crystalline HfO₂ powders were prepared by precipitation method using hafnium tetrachloride and sodium hydroxide as precursors. A series of hydraulic pressed pellets were formed to record the gas sensing characteristics of hafnia (HfO₂). XRD, micro-Raman, FESEM and EDXA techniques investigated the structural, morphological and compositional properties of the pellets while the electrical properties were studied by current-voltage measurement. The Brunauer–Emmett–Teller (BET) surface areas and pore sizes of HfO₂ powders were estimated by the nitrogen adsorption-desorption method and the XPS analysis showed the presence of oxygen vacancies inside HfO₂ matrix crucial for gas sensing applications. The gas sensor characteristics of hafnia at room temperature ambient were studied by employing ethanol gas at various concentrations. HfO₂ based sensors exhibited very high and linear response when exposed to ethanol gas. The HfO₂ based sensors can be utilized as a promising candidate for practical detectors of ethanol gas due to its room temperature operation, stability, reproducibility and excellent response–recovery properties.

Keywords

HfO₂ Nanocrystals, Precipitation method, Mesoporous nature, Ethanol gas detection

O7.01

Heterogeneous dynamics and Ordering of perylene layers on Ag(110)

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Abstract

We present a room temperature STM study of dynamics of flat lying perylene molecules shaping diffusive monolayers on Ag(110) driven by substrate site recognition. Thermal diffusion, balancing the intermolecular interaction and the site recognition, give rise to remarkable properties of the molecular layer. At low coverage the perylene liquid undergoes a first order dynamical phase transition. With molecule density increase the 2D liquid transforms from a short-range into a long-range ordered state. At monolayer regime close to saturation the molecules establish **a perfect long-range dynamic order** forming a thermodynamically stable network, built up from different sets of hydrodynamics modes. These results reveal a new type of interface state that we named « **epitaxial liquid** ». The monolayer persists the permanent substrate restructuring driven by silver ad-atom diffusion and is able to spread consistently over mono- and bi-atomic surface steps. Then, the heterogeneous dynamics bestows to the monolayer dynamics, characteristic to a liquid and long-range order characteristic to a crystalline solid. We anticipate that this duality, unattainable under conventional nanofabrication, opens perspectives to fabricate epitaxial self-assembled nanostructures of arbitrary lateral shape.

Keywords

Molecular layer, heterogeneous dynamics, epitaxial liquid

O7.02

Growth and electronic structure of nanostructured hexagonal boron nitride on curved crystals featuring a variable surface step density of vicinal surfaces

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Abstract

We report on the structural and electronic properties of hexagonal boron nitride (hBN) and graphene (Gr) grown on curved single crystal substrates of Pt and Rh close to the (111) face. Such curved crystal substrates feature an increasing density of surface steps. hBN and Gr growth lead to a re-organisation of the substrate forming stable facets overgrown by the respective 2D materials. On both substrate materials, we observe by low-energy electron diffraction and scanning tunnelling microscopy different stable facets that we explain by the strength of substrate-overlayer interaction and the lattice misfit. In the strong interacting substrate, Rh, the hBN “nanomesh” formation at the (111) face is altered and a new hBN/Rh(337) facet grows that forms nanostripped hBN areas [1]. Angle-resolved photoemission measurements reveal that the nanostripes give rise to electronic structure changes with minigap openings. On weakly interacting Pt, the hBN and Gr Moiré superstructures produce facets with slightly different chemical properties. Here, the weakest substrate-overlayer interaction occurs at the (111) facet. In the hBN/Pt and Gr/Pt cases, no nanostripe effects have been observed in the electronic band structure analysis.

[1] K. Ali *et al.*, *Adv. Sci.* **8**, 2101455 (2021).

Keywords

growth, electronic structure, hexagonal boron nitride, curved crystal substrates

O7.03

Germanene variant or weird surface alloy: an intriguing structure by Ge segregation through Au(111) thin films

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Abstract

In the late 60's ring-like LEED patterns observed from platinum surfaces heated in UHV were interpreted as resulting from rotationally disordered graphene/graphite sheets [1]. Upon mildly heating a thin gold film deposited at room-temperature onto a germanium (111) surface, a mysterious ringlike structure developing into 24 well defined spots was observed by LEED in the early 70's [2]. A first interpretation in terms of segregated germanium forming four epitaxial rotated germanene domains [3] on top of flat Au(111) islands [4] was initially proposed by analogy with the formation of germanene layers the other way around, i.e., upon *in situ* deposition of germanium onto bulky Au(111) single crystals [5]. Since then, other interpretations involving intermixing [6] and two-dimensional germanium-gold surface alloys were suggested [7].

Here, we re-investigate the segregated system, using a combination of several surface sensitive techniques from angular-resolved UPS to EDS, LEED and STM, and we discuss their related new results.

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[7] D. A. Muzychenko *et al.*, JETP Letters, 106, 217 (2017)

Keywords

2D materials, Germanene , Au(111), Segregation

07.04

2D networks through self-assembly of Pd-cyclometallate C₂₂H₁₄Br₂Cl₂N₂Pd₂ on Ag(110)

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Abstract

Cyclometallated complexes are attractive for numerous applications: catalysis, organic synthesis, and formation of biologically active compounds¹. Particularly, palladium complexes have been extensively studied for several catalytic cross-coupling reactions^{2,3}. Depositing such complexes on a metal surface is little explored and therefore fundamental understanding of their properties is lacking. In this context, we investigated the interaction of Pd cyclometallated compound [(2-[2-{3-bromopyridyl}] phenyl) palladium chloride tetramer] (C₂₂H₁₄Br₂Cl₂N₂Pd₂) with Ag(110) with the goal of exploiting their potential for the synthesis of ordered arrays of single metal atoms embedded in a carbon matrix. The choice of Ag(110) as a substrate due to its intermediate reactivity among coinage metals. The precursor was chosen for its planar structure and its thermal stability; moreover, brominated molecules dissociate on Ag surfaces at RT thus favoring the formation of new C-Ag or C-C bonds^{4,5}. The system is characterized upon RT deposition of the molecules and following annealing up to 150 °C by combining STM, NEXAFS and XPS measurements. The adsorption model is validated by ab-initio calculations and comparison with simulated STM images. Our results indicate a complex surface chemistry: the substrate promotes dissociation of the Pd cyclometallate into two fragments. Each fragment is coordinated by an Ag atom from the substrate while the Pd atoms diffuse into the subsurface. The dissociated halogen atoms bind to surface Ag atoms. Though the final configuration is not the one originally foreseen and is not optimal for further catalytic studies, it opens new possibilities for this class of materials.

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5 Smerieri, M. *et al. Nanoscale* 8, 17843–17853 (2016)

Keywords

Organometallics, palladium complexes, STM, DFT

07.05

Halogenated aromatic compounds on ag(110): Self-assembly and polymerization

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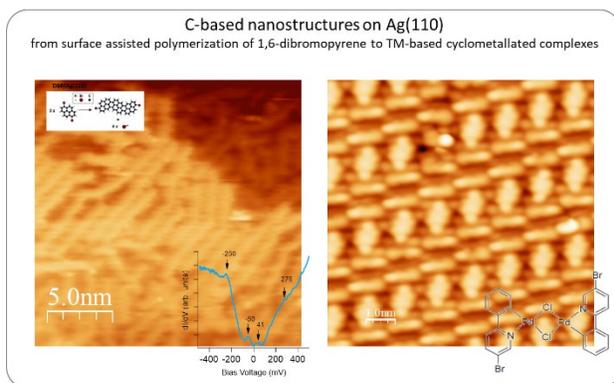
Abstract

It is now well established that the chemical and electronic properties of graphene and carbon-based nanostructures such as graphene nanoribbons (GNRs) can be modified and optimized for specific applications e.g. by modifying parameters such as the substrate material, the nature of the precursor molecules, the presence of dopants and other growing conditions [1][2].

While there are numerous studies of carbon-based nanostructures doped with non-metallic elements [1], certain systems such as cyclometallated complexes on metallic surfaces are less understood. Conversely, several theoretical works predict interesting catalytic properties for C-based nanomaterials doped with TM atoms.

Here we present the formation and characterization of C-based nanostructures forming by self-assembly of halogenated aromatic precursors on Ag(110). The use of halogenated compounds is crucial to the formation of intermolecular bonds thanks to the easy C-Br bond breaking at the surface. Characterization includes scanning tunnelling microscopy, X-ray photoemission spectroscopy and ab-initio calculations.

Firstly, we investigated the oligomerization of 1,6-dibromopyrene to form ordered arrays of **GNRs with alternate zig-zag and armchair edges. These structures are monodispersed in width** [3]. Their electronic band structure and their modifications upon oxygen exposure have been characterized by surface science methods [4]. Second, we moved to a more complicated system with cyclometallated compound complex Bis-[2-bromo-5-phenylpyridine] palladium, which contains two Pd atoms in the precursor molecule. In this case, interesting self-assembled patterns are observed upon deposition and subsequent annealing of the molecules. Though, compared to the simpler bromopyrene, no polymerization occurs for the cyclometallated molecules, interesting and unexpected chemistry is observed due to the interaction with the reactive Ag substrate.



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Keywords

graphene, self-assembly, nanostructures

07.06

Growing perfect graphene on a liquid metal: From self-assembled flakes to the single layer

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Abstract

The synthesis of large, defect-free two-dimensional materials (2DMs) such as graphene is a major challenge toward industrial applications. Chemical vapor deposition (CVD) on liquid metal catalysts (LMCats) is a recently developed process for the fast synthesis of high-quality single crystals of 2DMs. However, up to now, the lack of *in situ* techniques enabling direct feedback on the growth has limited our understanding of the process dynamics and primarily led to empirical growth recipes. Thus, an *in situ* multiscale monitoring of the 2DMs structure, coupled with a real-time control of the growth parameters, is necessary for efficient synthesis.

Here we report real-time monitoring of graphene growth on liquid copper (at 1370 K under atmospheric pressure CVD conditions) *via* four complementary *in situ* methods: synchrotron X-ray diffraction and reflectivity, Raman spectroscopy, and radiation-mode optical microscopy. This has allowed us to control graphene growth parameters such as shape, dispersion, and the hexagonal supra-organization with very high accuracy. Furthermore, the switch from continuous polycrystalline film to the growth of millimeter-sized defect-free single crystals could also be accomplished. The presented results have far-reaching consequences for studying and tailoring 2D material formation processes on LMCats under CVD growth conditions. Finally, the experimental observations are supported by multiscale modeling that has thrown light into the underlying mechanisms of graphene growth.

Reference:

“Real-Time Multiscale Monitoring and Tailoring of Graphene Growth on Liquid Copper” M. Jankowski, ¶ M. Saedi, *, ¶ F. La Porta, A. C. Manikas, C. Tsakonas, J. S. Cingolani, M. Andersen, M. de Voogd, G. J. C. van Baarle, K. Reuter, C. Galiotis, G. Renaud, O. V. Konovalov, and I. M. N. Groot*, ACS Nano 2021, **15**, 9638–9648

<https://doi.org/10.1021/acsnano.0c10377>

Keywords

graphene growth, liquid metal catalyst, in situ monitoring, Multiscale

O7.07

Effect of the crystallographic *c*-axis orientation on the tribological properties of the selected few-layer transition metal dichalcogenides

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Abstract

Transition metal dichalcogenides, a member of two-dimensional materials group, have received increased scientific attention thanks to their unique electronic, physical, and chemical properties. In this work, a comparative investigation of nanoscale friction behavior of MoS₂ and PtSe₂ layers with the in-plane (||) and out-of-plane (⊥) crystallographic orientation of the *c*-axis have been performed based on the structural, morphological, and wettability (contact angle, Θ) measurements. MoS₂ and PtSe₂ ultra-thin films were prepared by sulfurization and selenization of 3 nm magnetron pre-deposited Mo and Pt layers, respectively. The growth of the layers with a different *c*-axis orientation was controlled by changing the synthesis parameters during the thermal sulfurization/selenization process.

The rotation of *c*-axis from ⊥ to || shows a different impact on the nanotribological and morphological properties of MoS₂ and PtSe₂. In particular, ⊥ oriented MoS₂ shows more than six times lower friction and higher Θ in comparison with || oriented films. However, the identical change in the *c*-axis orientation for PtSe₂ caused an opposite trend in friction (it increased approx. by half) and almost unchanged Θ . Moreover, switching the *c*-axis from ⊥ to || is accompanied by an increased RMS roughness of MoS₂ and PtSe₂ surfaces (from 1.3 to 2.3 nm and 0.69 to 0.81 nm, respectively). Thus, the observed opposite nanoscale friction behavior can be a result of a different configuration of S and Se at the edges due to the different coordination of MoS₂ and PtSe₂ (2H and 1T, respectively).

This work was performed during the implementation of the project Building-up Centre for advanced materials application SAS, ITMS project code 313021T081 supported by Research & Innovation Operational Programme funded by the ERDF (50%) and Research and Development Agency under the contract no. APVV-17-0560.

Keywords

thin films, nanofriction, crystallographic orientation, contact angle

O7.08

Electronic structure of stable facets in the 2D material hBN/Pt system

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Abstract

We present the study of hexagonal boron nitride (hBN) grown on curved crystal substrates c-Pt, reporting the electronic structure properties of the stable facets. We encountered (111), (110), (221) and (552) as stable facets, studied by low-energy electron diffraction (LEED) and scanning tunnelling microscopy (STM).

The electronic structure was characterized by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS). We observed that the hBN/Pt(111) system is the weakest interacting overlayer system, contrary to the side facets which are strongly bound to the c-Pt substrate.

Additionally, we determined using Angle-resolved photoemission measurements (ARPES), a π^* band energy shift around (1.3 eV) due to the changed hBN/c-Pt interaction between the electronic bands at (111) and (110) facets.

Keywords

curved crystal, stable facets, hBN/Pt, electronic structure

O7.09

Tunnelling states in heterogeneously coupled SK-SML quantum dot devices

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Abstract

Vertical coupling of Stranski – Krastanov (SK) QD layers, presents enormous benefits on the performance of the optoelectronic devices by drastically enhancing the coherence, but as a shortcoming, cumulative strain propagates through these structures and causes inhomogeneity, defect formations, and In-Ga interdiffusion. These effects limit the number of stacks in the heterostructure. On the other hand, heterostructures with Submonolayer (SML) QDs have lesser strain and higher confinement, but the size of dots is smaller in comparison with SK QDs. Heterogenous coupling of these two types of dots could provide the solution for the strain, as well as enhances device performance by electronic energy state coupling. Heterostructures are grown with ten repetitions of coupled SK on SML and SML on SK QD layers with varying GaAs spacer of 7.5 nm and 20 nm in between them. Low-temperature photoluminescence (PL) and photoluminescence excitation (PLE) measurements are performed for the optical characterization of the samples. Distinguished peaks of SML QDs (960 - 980 nm) and SK QDs (1050 -1070 nm) are observed for the structures with 20 nm separation, but the SML peaks vanish for the samples with lower separations (7.5 nm). The ground state of SML QDs and the excited state of SK QDs are found to be coinciding, which was observed through power-dependent PL, deconvolution of PL peaks, and PLE results. An increase in tunneling through these resonating states in samples with lower separation is thought as the reason for the vanishing SML peak in the PL spectra. These resonating states will provide better absorption of light for intra-band transitions.

Keywords

Tunnelling States, Heterogeneously-coupled Quantum Dots, Photoluminescence, Photoluminescence Excitation

O8.01

Bio-mimicked surfaces with adjustable nanoarchitecture – new efficient separation materials with mitigated fouling

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Abstract

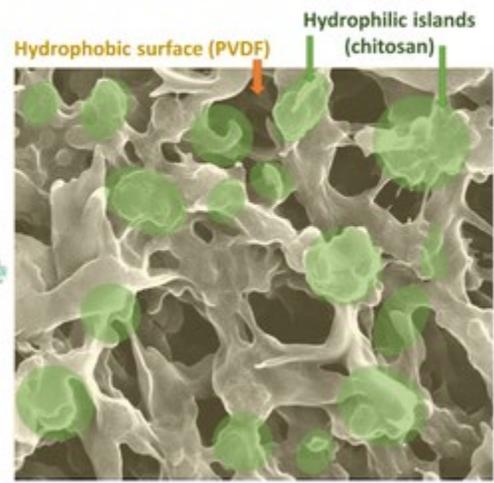
As water scarcity has become a major global problem, fog-harvesting technologies are considered a current sustainable solution for water resources. Such a solution has been adopted by material science and subsequently membrane science as well. The design, characterization, and application of efficient biomimetic membranes have been presented. The idea of hybrid hydrophobic/hydrophilic separation materials was mimicked from *Stenocara gracilipes* beetle, an animal living in the Namib desert that can maintain life by capturing atmospheric water from fog. Hydrophobic surface with a hydrophilic pattern generated by chemical attachment of chitosan to the poly(vinylidene fluoride) (PVDF) activated and silanized surfaces. The membrane morphology and surface chemistry were studied by implementing a series of analytical techniques which proved the covalent and durable attachment of chitosan to the polymeric matrix. As a result of chitosan attachment, significant enhancement in transport and separation was reported. Pristine PVDF was characterized by a water flux of $5.28 \text{ kg m}^{-2} \text{ h}^{-1}$ and activation energy of $48.16 \text{ kJ mol}^{-1}$. The water flux and activation energy for a hybrid membrane with chitosan were equal to $15.55 \text{ kg m}^{-2} \text{ h}^{-1}$ and $33.98 \text{ kJ mol}^{-1}$, respectively. Moreover, the membranes were tested in the removal of volatile organic compounds, presenting impressive improvement in separation and transport when the hybrid materials were applied. The process separation index increased from $\sim 6.8 \text{ kg m}^{-2} \text{ h}^{-1}$ to $90 \text{ kg m}^{-2} \text{ h}^{-1}$ for pristine and hybrid-material, respectively. Finally, separation materials were used in the juice concentration process when the fouling study was done as well. The normalized flux decline for pristine PVDF was $\sim 50\%$, whereas for hybrid material below 10%.

The research was supported by 2017/26/D/ST4/00752 (Sonata 13) grant from the National Science Centre Poland, Poland.

Biomimicry - Hydrophobic surface with hydrophilic islands



Bioinspired membranes



Keywords

chitosan, PVDF, biomimicry, functionalization

O8.03

Novel and low cost-effective and magnetic hybrid material for CO₂, CH₄, and N₂ adsorption

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Abstract

Magnetic materials were synthesized from sugarcane bagasse with magnetite nanoparticles. This magnetic material was the support of a Metal-Organic Framework (HKUST-1) to synthesize the magnetic composite ([MOF@MB]). The chemical and physical characteristics of the final composite were carefully studied by SEM, BET, TGA, FTIR, and XRD. [MOF@MB] was tested for CO₂, CH₄, and N₂ capture at different pressures. The characterization showed that there are morphological differences in the surface of material despite their similarities in terms of functional groups. The surface area of [MOF@MB] was 45.70 m² g⁻¹. In the X-ray diffractogram, the formation of the magnetite nanoparticles and the MOF were observed in the composite. The results showed that the affinity for CO₂ is more significant than for the other two tested gases. With the low content of HKUST-1 and magnetite nanoparticles on waste material, the composite develops a significant adsorption capacity. The CO₂ maximum adsorption capacity was 8.629 mmol g⁻¹ for bagasse shell magnetic composite. The capture of CO₂ was carried out through multilayer adsorption on the heterogeneous surface and a combination of mechanisms.

Keywords

sugarcane bagasse waste, magnetite nanoparticles, CO₂ capture, HKUST-1

O8.04

MOF derived visible light photocatalyst for simultaneous degradation and hydrogen production from wastewater

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Abstract

Growing energy demands and environmental remediation have gained top priority in the research field worldwide. The limited availability of fossil fuels has steered the wheel towards clean and renewable energy sources. Taking into account the global clean energy demand, a novel photocatalyst based on a metal-organic framework (MOF) and cerium dioxide nanoparticles (CeO_2) was synthesized to perform photocatalytic water splitting reactions. The resulting composite (Carbonized CeO_2 @MIL-53 nanocomposite, MIL: Matériaux de l'Institut Lavoisier) was characterized by using standard analytical methods (XRD, BET, FTIR, UV-DRS, SEM, EDS, photoluminescence spectroscopy) to estimate the crystal size, surface area, pore volume, functional groups, band gap, morphology, and charge separation in the synthesized nanocomposite. At the same time, there is increasing concern about effluent discharge into natural water systems, which has serious environmental and human health implications. Thus, it is essential to treat wastewater and turn it into valuable commodities. The effluent was obtained with the help of a dye industry in Mumbai (India). The simultaneous degradation of real-time industrial effluent and hydrogen production was carried out using a batch photochemical reactor. After 180 minutes of irradiation, the photocatalytically active carbonized CeO_2 @MIL-53 nanocomposite produced hydrogen without using any sacrificial agents. The corresponding hydrogen evolution rate was evaluated, which was observed to be many times higher than the pristine materials. The remarkable photoactivity was due to the high surface area, superior charge separation property, and less recombination of the charge carrier pair in the carbonized CeO_2 @MIL-53 nanocomposite. Furthermore, the photocatalyst exhibited excellent reusability for hydrogen production for up to 5 consecutive cycles. The kinetics and underlying mechanism was studied. The results show techno-economic feasibility of carbonized CeO_2 @MIL-53 nanocomposite for practical applications.

Keywords

MOF composite, Water splitting, Photocatalysis, hydrogen production

O9.01

Gas-solid interactions in porous thin oxide films investigated by near-ambient pressure XPS

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Abstract

An interesting aspect of performing XPS in the presence of a gas is that the energy levels of the gas molecules are naturally referenced to their vacuum level, and not to the Fermi level of the spectrometer. As a consequence, the measured binding energy of core level gas molecules is very sensitive to surface properties, such as for example, variations in work function [1]. In this work we exploit this effect and we apply it to the investigation of SiO₂ thin films, chemically identical, but very clearly differentiated in terms of surface roughness and internal porosity [2]. The films were investigated by XPS at 1 and 5 mbar N₂ pressures and the core levels of both surface species and gas molecules were measured. The binding energy of the N1s core level line showed a clear dependence with the surface properties of the sample (in terms of roughness and porosity), while the line FWHM was correlated to the surface charging of the films. The origin of both observed effects and the information they provide about the surface will be discussed. Our results indicate that XPS analysis of the environmental gas is a sensitive tool to probe surface characteristics that go beyond standard chemical characterization by XPS.

This work was supported by the German Research Foundation (DFG) within the framework of the Transregional Collaborative Research Center TRR 87/1 (SFB-TR 87) "Pulsed high power plasmas for the synthesis of nanostructured functional layers".

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Keywords

XPS, Near ambient pressure, porous thin films

O9.02

Characterization of galvanic silver dispersion coatings with optimized electrical and tribological behavior

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Abstract

The use of contact lubricants for current-carrying plug connections is the common standard technology in electrical power engineering. The aim of the project is to develop a galvanic silver dispersion coating with self-lubricating properties as an alternative. The particles, in the form of powders, are dispersed into a metal matrix electrolyte and kept in suspension by appropriate electrolyte circulation. The particle incorporation into the silver layer can be controlled by a suitable choice of process and electrolyte parameters [1]. Within the scope of this project, it was possible to incorporate various particles of known solid lubricants (graphite, hBN, SiC, MoS₂, WS₂, Bi₂S₃ and SnS) into a silver matrix electrochemical deposition [2-3]. Ag-graphite was used as a reference system for evaluating the friction and wear behavior of the other particles. The dispersion depositions with hBN, SiC, Bi₂S₃ and SnS showed no significant improvement of the co-efficient of friction compared to pure silver. Only MoS₂ and WS₂ particles improved the tribology properties of the silver particle dispersion depositions by a significant amount, with co-efficient of friction 0.32 and 0.26 respectively. In addition to the co-efficient of friction, the surface wear was also analyzed with light microscope comparisons and confocal microscopy 3D representations.

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Keywords

dispersion coating, electrochemical deposition, silver, tribology

O9.03

In situ infrared spectroscopy for quantitative characterization of palladium hydride nanoparticles

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Abstract

The main purpose of this work is to turn infrared spectroscopy to the tool for quantitative structural characterization of nanomaterials which was exemplified on a palladium hydride nanoparticles. Fourier transform infrared spectroscopy (FTIR) is widely applied to characterize the type of surface metal sites using CO as a common probe molecule. We propose a method in which precise characterization of the positions, intensities, and the widths of the FTIR peaks is used to characterize quantitatively the structural and electronic changes in the nanosized object. This was successfully demonstrated for palladium hydride nanoparticles where FTIR was used to obtain pressure-composition isotherms, i.e. determining the H/Pd ratio as the function of partial hydrogen pressure at selected temperatures. Experimental data were collected in situ in a DRIFTS mode. The region corresponding to the CO vibrations was deconvoluted and the database of key features characterizing this part of spectrum was constructed, some of which appeared to be in a perfect correlation with the data collected by X-ray diffraction and hydrogen chemisorption under similar conditions. Machine learning algorithms were applied to select best spectral descriptors, which are sensitive to H/Pd ratio. The results were also supported by theoretical quantum chemical calculations demonstrating the effect of Pd-Pd interatomic distances and H/Pd ratio on the vibrational spectra of absorbed CO molecules.

The authors acknowledge the Ministry of Science and Higher Education of the Russian Federation for financial support (Agreement № 075-15-2021-1363)

Keywords

FTIR, Pd nanoparticles, ML

O9.04

Spin-Resolved ARPES through Topological Transition in $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ (111) Epilayers

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Abstract

Topologically protected helical spin texture on the surface of topological insulators makes these materials attractive for application in spintronics [1]. Topological crystalline insulators (TCI) based on the narrow gap lead-tin chalcogenide IV-VI semiconductors provide a unique platform for studying topological phase transitions as a function of external perturbations [2]. Here we report on angle- and spin-resolved photoemission (SR-ARPES) experiments of TCI $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ epilayers grown by molecular beam epitaxy in (111) orientation. High surface quality of obtained samples is proved by RHEED and AFM. The Sn content is determined using XRD and EDX-SEM technique. The samples of trivial and topological composition are transferred to SOLARIS synchrotron for ARPES studies using an ultra-high vacuum suitcase to protect their surface from degradation. $E(k)$ ARPES spectra and spin-resolved energy dispersive profiles were recorded in photon energy range of 50-90 eV. The topological transition is observed as a function of Sn content and temperature. Helical spin polarization is present not only for samples of topological composition but also for trivial ones (with open band gap) (Fig.1). Spin polarization of 30 % is achieved for in-plane spin component and nearly absent for out-of-plane one. It is found that if topological surface states overlap with bulk ones the observed spin polarization is diminished drastically. The obtained knowledge paves way to application of surface states not only of topological but also trivial IV-VI semiconductors in spin-charge conversion devices.

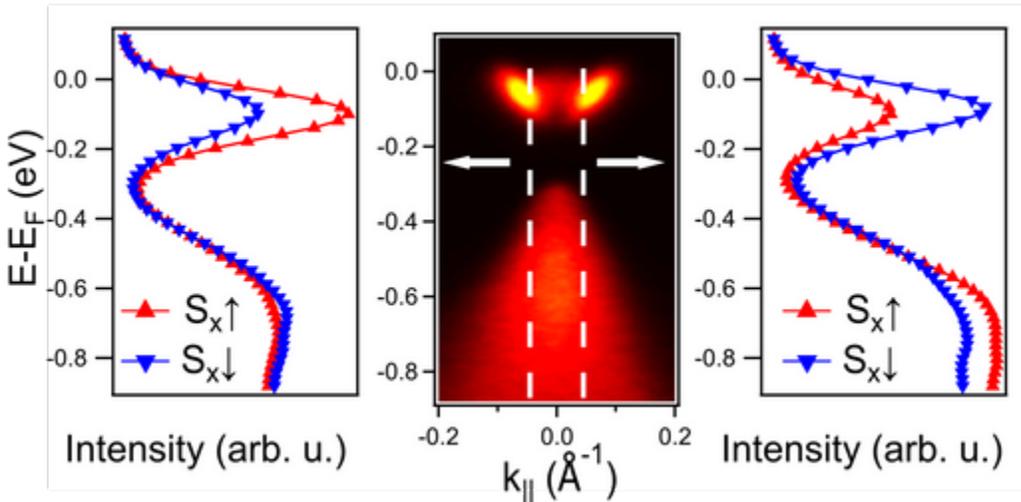


Fig.1. ARPES image and corresponding spin-resolved EDC profiles for trivial $\text{Pb}_{0.88}\text{Sn}_{0.12}\text{Se}$ epilayer

Acknowledgements: The work is supported by the Foundation for Polish Science through the IRA Programme co-financed by EU within SG OP. We thank NSRC SOLARIS for beamtime allocation.

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Keywords

Photoemission spectroscopy, Molecular beam epitaxy, Topological crystalline insulator

Poster Sessions:

P1.01

Laser irradiation-induced phase transition in titanium dioxide films

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Abstract

The oxidation of titanium substrates in the air under laser irradiation is investigated. The experimental dependence of TiO₂ layer thickness on the number of laser pulses is subjected to the comprehensive analysis. The prevailing chemical and physical processes on the substrate surface and in the near-surface layer are determined. It is found that the laser irradiation drives the surface energy induced mixing in the near-surface layer of titanium substrates. The mixing rate sharply depends on temperature. This allowed to detect the exothermic phase transition from anatase to rutile in the titanium dioxide films using ex-situ experimental measurements.

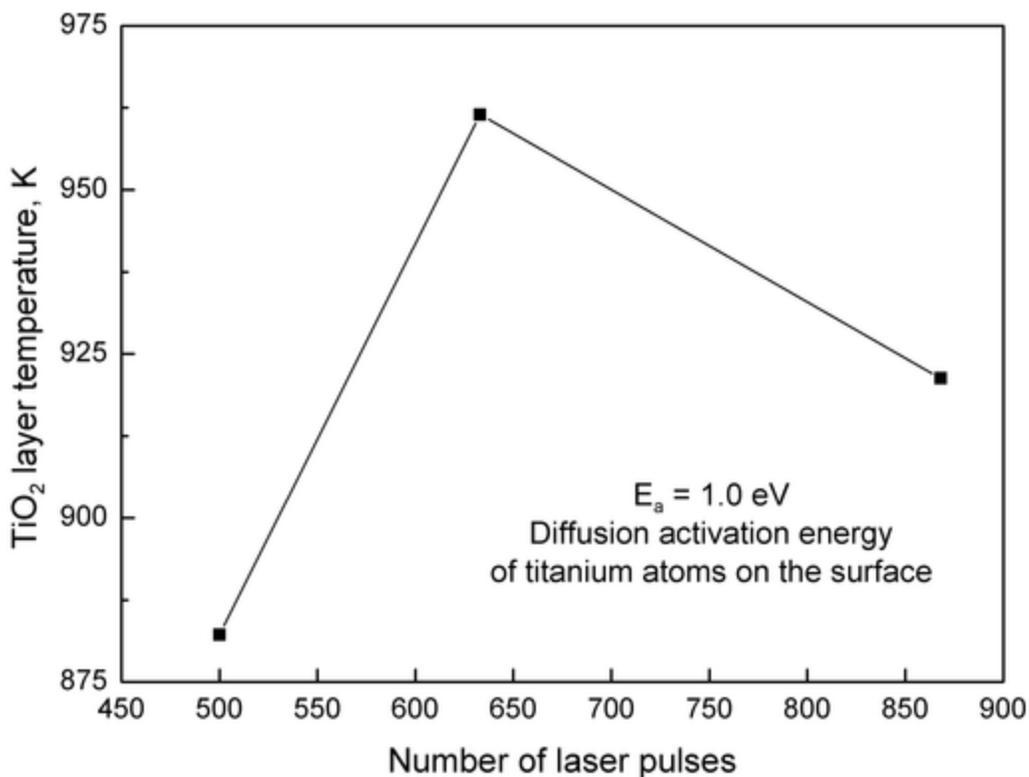


Fig. 1. Theoretical dependence of TiO₂ layer temperature on the number of laser pulses.

Keywords

Titanium dioxide, Phase transition, Laser irradiation

P1.02

Formation of graphene on SiC surface at elevated temperatures

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Abstract

The formation of graphene on SiC substrates is investigated theoretically. At elevated temperatures thermal decomposition of SiC molecules is followed by subsequent desorption of formed Si atoms. This creates the adsorbed layer consisting of C atoms required for graphitization reactions on the SiC surface. Quality of the obtained graphene is characterized by the number of C atoms in the average graphene sheet and the graphitization degree. It is found that the graphitization degree increases with the increase in thermal decomposition of SiC molecules. High quality graphene is obtained when the removal of C atoms from the adsorbed layer is reduced to minimum.

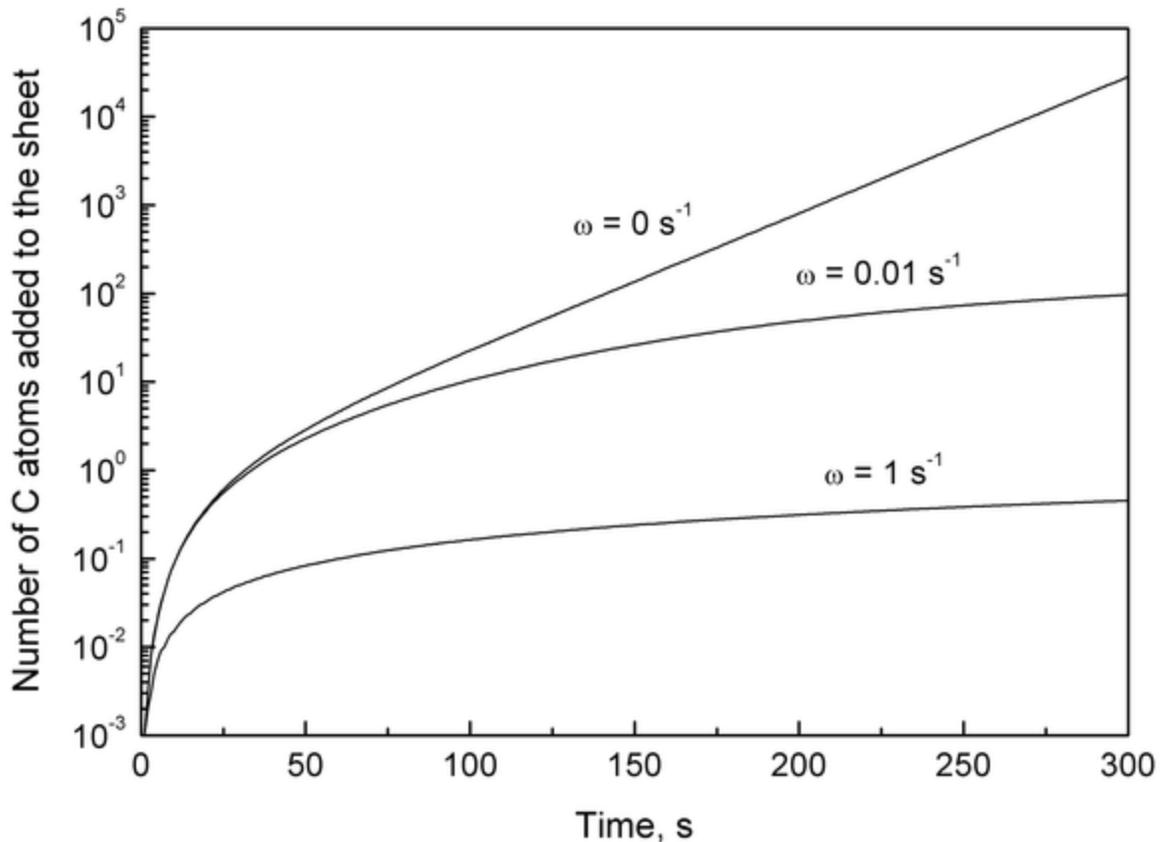


Fig. 1. The evolution of graphene sheet at different frequencies of C atom removal from the adsorbed layer.

Keywords

SiC, Thermal decomposition, Graphene

P1.03

Surface Li effects on the electronic properties of GaAs nanowires: A first principles approach

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Abstract

In recent years the search for better anode materials for Li-Ion batteries has been one of the most researched topics, due to the potential of these batteries in helping to overcome the shortcomings of renewable energy sources. One interesting candidate to this end is GaAs which is a material that has been widely used in microelectronics industry. However, its potential for the development of better anodes of Li-ion batteries has seldom been explored. Also, the prospect of GaAs nanowires for this application is of interest due to the high surface area that the nanowires have that could allow for an increased quantity of Li to be adsorbed increasing battery capacities. In this work the effect of Li on the electronic properties of GaAs nanowires was studied using a first principles Density Functional Theory, and the supercell schemes. The nanowires were modelled by removing atoms outside a circumference from an otherwise perfect GaAs crystal, in the [111] direction, where all surface dangling bonds were passivated with H atoms. To study the effect of Li on the nanowire surface H was replaced with Li gradually thus conforming an hybrid H+Li passivation scheme. The results show that the Li at first passivates the surface bonds of the GaAs nanowires since there is still a band gap with a hybrid H+Li passivation scheme. However, as the number of Li increases and the passivating H decreases the metallic nature of the Li becomes predominant and the nanowires become metallic. These results give a first insight that the nanowires could be viable for the development of Li-ion batteries, as the electronic conduction improves with the lesser band gap.

Keywords

DFT, GaAs Nanowires, Electronic Properties, Lithium batteries

P1.04

Effects of surface on the mechanical properties of nanoporous SiC

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Abstract

Nanoporous Silicon Carbide is an interesting material due to its multiple potential applications, as H sensors, anodes for energy storage, UV detectors among others. Even when there have been multiple theoretical and experimental investigations on the properties of nanoporous SiC, seldom study its mechanical properties, and even less the effect of the Si/C ratio in said properties. The mechanical properties are of the utmost importance for the potential application of nanoporous SiC since it is crucial to determine which factors alter the natural mechanical characteristics of SiC such as its high hardness. In this work we study the effects of the surface Si/C ratio on the mechanical properties of nanoporous SiC using the first principles density functional Theory and the supercell scheme. The porous structures were modelled by removing columns of atoms on the [001] direction from an otherwise perfect 3C-SiC crystal, where the pore morphology was chosen so that the surface of the pore was constituted only of C (C-rich) or Si (Si-rich) atoms, where the surface dangling bonds are passivated with H atoms. The results show that the mechanical properties of the nanoporous structure are, in fact, influenced by the prevalence of either C or Si on the pore surface. The C-rich pores show higher young and bulk modulus, probably due to the weaker Si-H bonds in the surface passivation of the porous structure. These results show that a study of the surface is crucial for the engineering of the mechanical properties of porous SiC.

Keywords

Porous Silicon Carbide, DFT, Mechanical Properties, Surface passivation

P1.05

Salicylic acid-functionalized N-doped TiO₂ nanoparticles for visible-light photocatalytic degradation of ciprofloxacin

Ansaf V. Karim, Sukanya Krishnan, Amritanshu Shrivastav

Indian Institute of Technology Bombay, Mumbai, India

Abstract

The visible-light photocatalytic degradation potential of TiO₂ nanoparticles is limited owing to their higher bandgap, limited adsorption capability and higher charge recombination rates. Surface modification techniques can improve the photocatalytic properties of TiO₂ catalyst for photocatalytic applications. In this study, the application of surface-modified TiO₂ particles for the degradation of a model pollutant, Ciprofloxacin (CPX) under visible light was studied. TiO₂ particles were doped with nitrogen using a sol-gel method followed by functionalization with salicylic acid to synthesis salicylic acid-functionalized N-TiO₂ (SA-N-TiO₂) catalyst with a molar ratio of Ti:N of 1:1 functionalized with 0.1 wt% of SA. The synthesized particles were characterized with XRD, TEM, FTIR, XPS, PL, UV-DRS and point of zero charge techniques. A preliminary photocatalytic degradation study conducted at a baseline condition of natural solution pH 5.2, catalyst dosage of 0.5 g L⁻¹ and initial CPX concentration of 10 mg L⁻¹ resulted in 44% degradation with SA-N-TiO₂ when compared to 37% and 20 % respectively with N-TiO₂ and TiO₂ under blue LED light irradiation for 2h. The enhancement in the photocatalytic performance of SA-N-TiO₂ could be attributed to the formation of mid-bandgap due to N incorporation and functionalization enhancing the availability of more electrons on the surface and improving the visible light absorption of the catalyst. Further, the influence of catalyst dosage, pH value, and CPX concentration on the degradation were investigated. Finally, the reuse potential of the catalyst and possible degradation mechanism was proposed.

Keywords

Doping, Surface Functionalization, Photocatalysis, Ciprofloxacin Degradation

P1.06

Development of visible light-responsive TiO₂ nanoparticles by natural chlorophyll pigment sensitization and N doping modification approaches

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Abstract

The development of visible light-active photocatalysts for the treatment of organic contaminants has attracted tremendous research interest in the past decades. The most commonly used semiconductor photocatalysts TiO₂ nanoparticles with wide bandgap have been reconstructed by several surface modification techniques, such as metal and non-metal doping, dye-sensitization, and heterogeneous composites, etc. Thereby, the TiO₂ catalysts can be effectively utilized under visible/solar light irradiation. In the present study, the combined effect of two types of modifications viz. non-metal doping and natural dye-sensitization on TiO₂ catalysts has been comprehensively investigated. The non-metal N doped TiO₂ was prepared via the sol-gel process followed by the sensitization with natural chlorophyll (Chl) pigments in the ratio of 0.1:1:1 (Chl:N:Ti) by wetness impregnation method. The prepared catalyst was comprehensively characterized with XRD, FTIR, TEM, PL, UV-Vis DRS, point of zero charges, and XPS. The photocatalytic efficiency of chlorophyll sensitized N doped TiO₂ was examined by the degradation of model contaminant ciprofloxacin (CPX) antibiotics. A preliminary study conducted at a baseline condition of natural CPX solution pH of 5.2, catalyst dosage of 0.5 g L⁻¹, and initial CPX concentration of 10 mg L⁻¹, with chlorophyll sensitized N-TiO₂ (Chl/N-TiO₂) resulted in 45% degradation when compared to 35% and 24 % respectively with N-TiO₂ and TiO₂ under blue LED irradiation for 150 minutes. The N doping leads to the formation of mid-gap energy level by shifting the valance band of TiO₂ whereas natural chlorophyll dye adsorbed on the surface of N-TiO₂ acts as the photosensitizer and donates electrons to N-TiO₂ which further improves the visible light photocatalytic degradation of contaminants. Further, the study comprehensively investigates the various operational parameters affecting the process and also understands the synergistic effect and the mechanism of natural dye-sensitization and N doping techniques.

Keywords

Doping, Dye-sensitization, Natural chlorophyll pigment, Visible Light Photocatalysis

P1.07

From petal-like to lotus-like materials – functionalized rare metal oxides as novel fillers for membrane-bases separation materials

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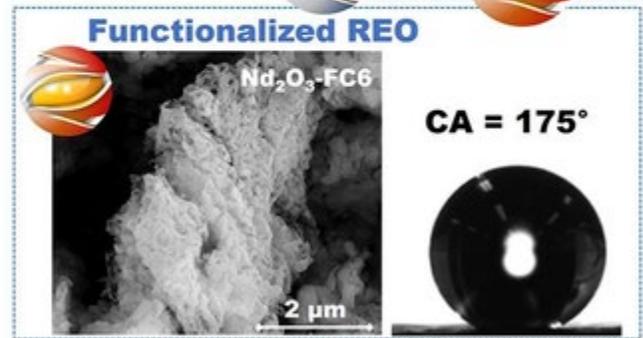
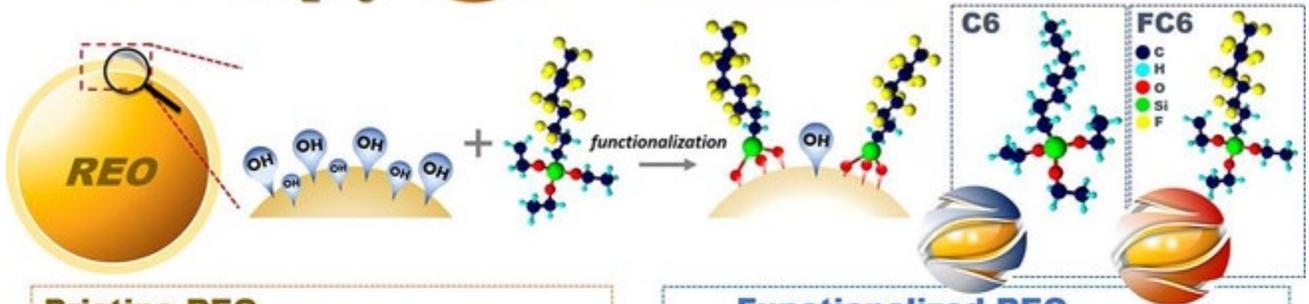
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Abstract

The easy and highly effective bioinspired method allowing to switch material properties from petal effect to lotus one in the one-step procedure has been developed. Thus, highly hydrophobic and superhydrophobic materials with adjustable adhesive features and fractal-like structures were successfully generated with high efficiency (67–84%). The work's essence was to modify chemically selected powders of lanthanide oxides (CeO_2 , Pr_6O_{11} , Nd_2O_3 , and Gd_2O_3). High effectiveness of the functionalization process with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FC6) and n-octyltriethoxysilane (C6) was proven by various techniques, *e.g.* XPS, HR-TEM, ATR, XRD, zeta potential. Materials with water contact angle between 143.6° (CeO_2 -C6) and 175.5° (Nd_2O_3 -FC6) with thermally stable nanolayer (up to 380°C) were generated. Surfaces functionalized with FC6 possessed a polar component of surface free energy (SFE) close to zero. Water behavior in contact with the modified materials was studied, taking into consideration the unique electron structure of lanthanides assessed by goniometric measurement, also adhesion and spreading pressure were determined. Very low adhesion and polar SFE partly resulted in immediate bouncing of water droplet upon contact with the modified surface. The presented method allows preparing stable materials with a high potential in materials chemistry and modulation of surface features and engineering (*e.g.* heat transfer fluids, specific coating).

CeO_2 Pr_6O_{11} **Rare Earth Oxide (REO)**
 Nd_2O_3 Gd_2O_3

- Petal effect (high adhesion)
- Hydrophobic



- **Petal effect**
- **Hydrophobic**
- **High adhesion**

One step procedure

- **Lotus effect**
- **Superhydrophobic**
- **Very low adhesion**
- **Fractal structure**

Keywords

lanthanide oxides, petal and lotus effect, superhydrophobicity, fractal structure

P1.08

Synergy between roughness and material chemistry to enhance transport and separation features of PVDF-based bio-hybrid separation materials

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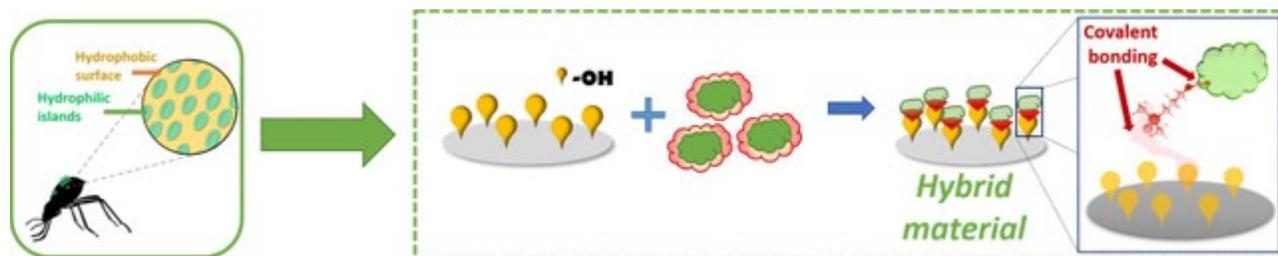
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Abstract

Highly efficient, hybrid separation materials for water purification were generated following a bioinspired system available in nature. The desert beetle (*Stenocara gracilipes*) was the inspiration for the formation of separation materials. Applying the hydrophobic poly(vinylidene fluoride) (PVDF) material as the substrate, the membrane was first activated and then functionalized with silane-based linkers, and the covalent anchoring of chitosan was successfully performed. The obtained surface architecture was a copy of the desert beetle's armor possessing a hydrophobic matrix with hydrophilic domains. The modification was done to adjust easily the wettability, roughness, and chemistry of the materials as well as adhesive properties. The membrane morphology and surface chemistry were studied by applying a series of analytical techniques. As a result of chitosan anchoring, substantial improvement in transport and separation was reported. Pristine PVDF was characterized by a water flux of $5.28 \text{ kg m}^{-2} \text{ h}^{-1}$ and activation energy of $48.16 \text{ kJ mol}^{-1}$. The water flux and activation energy for a hybrid membrane with chitosan were equal to $15.55 \text{ kg m}^{-2} \text{ h}^{-1}$ and $33.98 \text{ kJ mol}^{-1}$, respectively. The hybrid materials possessed enhanced stability and water resistance that were maintained after 10 cycles of membrane distillation tests.

ACKNOWLEDGMENT

The research was supported by 2017/26/D/ST4/00752 (Sonata 13) grant from the National Science Centre Poland, Poland.



Keywords

PVDF, material features, functionalization, separation

P1.09

Evolution of the electronic and crystallographic structure of thin film photoanodes deposited by reactive rf magnetron sputtering from Ti target under controlled O₂/Ar atmosphere

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Abstract

Titanium dioxide thin films are the most studied materials in the surface science. They are applied in solar cells, photoelectrochemical devices and become important in heterogenous photocatalysis. Specifically, TiO₂ is efficient as a photoanode in water photolysis, promoting hydrogen generation using solar radiation. Although absorption of TiO₂ is the highest in UV range of electromagnetic spectrum, modification of its anionic sublattice seems to be promising for an efficient performance at longer wavelengths, i.e., visible range. Such tailoring can be executed by changing the O₂/Ar ratio in gas atmosphere during reactive sputtering, finally leading to the film non-stoichiometry.

In this work, titanium oxide thin films were obtained by radio frequency magnetron sputtering of Ti metallic target in the O₂+Ar atmosphere, where the total gas flow was kept constant at 40 sccm but the O₂/(O₂+Ar) ratio varied intentionally from 0 to 30%. Power density during sputtering had to be increased from about 10 W/cm² to 12 W/cm² as O₂/(O₂+Ar) ratio changed from 0 to 30% because of the target poisoning effect.

X-ray diffraction results revealed that with the increase in the O₂/Ar ratio, phase composition changed from hexagonal Ti, Ti₂O₃ and rutile at low values to anatase at higher values. X-ray absorption spectroscopy XAS was applied to determine the influence of O₂/Ar ratio on the electronic structure of thin films. Titanium L₂₃ and oxygen K absorption edges were recorded using synchrotron radiation at SOLARIS National Synchrotron Radiation Centre, Kraków, Poland. Spectral dependence of absorption coefficient used for band gap analysis was based on the transmittance and reflectance measurements performed by means of UV-Vis-NIR spectroscopy. Scanning electron microscopy SEM allowed to observe systematic changes in films morphology.

The ultimate aim of these studies is application of efficient photoanodes in photoelectrochemical cells for hydrogen generation.

Research financed by NCN Poland, decision no. UMO-2020/37/B/ST8/02539.

Keywords

TiO₂, thin film photoanodes, XAS, synchrotron radiation

P1.10

Development of a novel modified electrochemical sensor SPCE/Nb₂O₅/CB for direct determination of glyphosate

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Abstract

Glyphosate (GLY, N-(phosphonomethyl)glycine) is a non-volatile and water-soluble chemical, one of the most widely used herbicides in agriculture to control weeds in various agricultural crops. This pesticide inhibits the biosynthetic pathway of aromatic amino acids essential for plant growth. In animals, many recent works suggest that glyphosate affects the regulation of the cell cycle, causing kidney and reproductive problems, in addition, a study demonstrated the toxicity of this herbicide for bees¹. In 2015, the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) drew attention to its toxicity and classified it as a potential carcinogen to humans². The disorderly use of glyphosate combined with its persistence in the environment and toxicity to animals and insects requires the development of sensitive analytical methods for the determination of glyphosate. Several analytical methods, including electrochemical, have been used for the determination of glyphosate, but there are few direct determination methods. Electrochemical sensors based on different nanomaterials have operational ease, miniaturization and automation potential, low cost, high sensitivity and low analysis time³. In this work, the properties of carbon black (CB) and niobium oxide (Nb₂O₅) nanoparticles were combined in the construction of a screen-printed carbon sensor (SPCE) applied to the direct electrochemical determination of the herbicide glyphosate by means of differential pulse voltammetry (DPV) in BR buffer pH 5.0 in a linear range of 2.49 to 29.1 ng mL⁻¹ with a limit of detection (LOD) 13.01 ng mL⁻¹.

Keywords

electrochemical sensor, screen printed carbon electrode, niobium nanoparticles, glyphosate

P1.11

Alternative synthesis of reduced graphene oxide

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Abstract

An essential requirement for the mass-production of graphene materials is their low cost. The present work demonstrates a low-cost synthesis route of reduced graphene oxide (rGO). A simplified Hummers method for the synthesis of graphene oxide (GO), without the use of NaNO_3 and/or H_3PO_4 , was applied using graphite flakes with unordered large size (75% over $150\ \mu\text{m}$). The inexistence of toxic gasses ($\text{NO}_2/\text{N}_2\text{O}_4$) and soluble ions ($\text{Na}^+/\text{NO}_3^-$) preserved the environmental duty of GO production. The mass-production of rGO was obtained after thermal process in vacuum. The low energy consumption ($250\ ^\circ\text{C}$ for 1 h) and the absence of any agents, such as argon/nitrogen, minimized the whole synthesis cost. The properties of GO and rGO were characterized with scanning electronic microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction spectroscopy (XRD), energy dispersive X-ray spectroscopy (EDS), attenuated total reflective Fourier transform infrared spectroscopy (ATR-FTIR), N_2 porosimetry, and UV-Visible spectrophotometry. The synthesized GO presented high specific surface area ($\sim 72\ \text{m}^2/\text{g}$). The obtained rGO was embodied to chitosan-based polymers acting as filler.

Keywords

Graphene oxide, Synthesis, Reduction, Characterizations

P1.12

The effect of boron and vanadium addition on the structure and properties of AlCrN coating

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Abstract

Coatings produced by physical vapour deposition are recognised as one of the very interesting premium technologies for the protection and modification of products surfaces due to the real possibility to synthesise materials with unique physical and chemical properties. One of the most effective coatings of this type is the AlCrN hard coating. AlCrN coatings have been developed for high-temperature wear applications, such as cutting tools or die casting moulds, due to their unique mechanical properties and oxidation resistance. The review of the state of knowledge in the field of AlCrN coatings produced by physical vapour deposition technique indicates that not fully used all the technological possibilities associated with the optimization of the chemical composition of this type of coatings. Perspective from the point of view of increasing the mechanical and tribological properties, it seems appropriate to introduce additions in the form of boron (B) and/or vanadium (V) to the AlCrN coating.

The AlCrBN, AlCrVN and AlCrVBN coatings were deposited in the arc plating PVD unit PLATIT π1511. Tests using the TEM and HRTEM confirmed a nanocrystalline structure of the investigated coatings. Based on the XRD analysis, the fcc type of the crystal structure was proposed for that coatings. The chemical bonding of particular elements in the tested coatings was evaluated by XPS. In sliding dry friction conditions, the investigated coatings reveal high wear resistance. The coatings demonstrated a dense cross-sectional morphology as well as good adhesion to the substrate. Compared to previous work, the modification of the chemical composition of the AlCrN coating by the addition of boron and vanadium increases its mechanical and tribological properties compared to the addition of silicon or titanium currently used.

Keywords

AlCrVBN, PVD, HRTEM, XPS

P1.13

ZnO-doped RE metal oxides self-cleaning coatings manufactured via spin-coating technique

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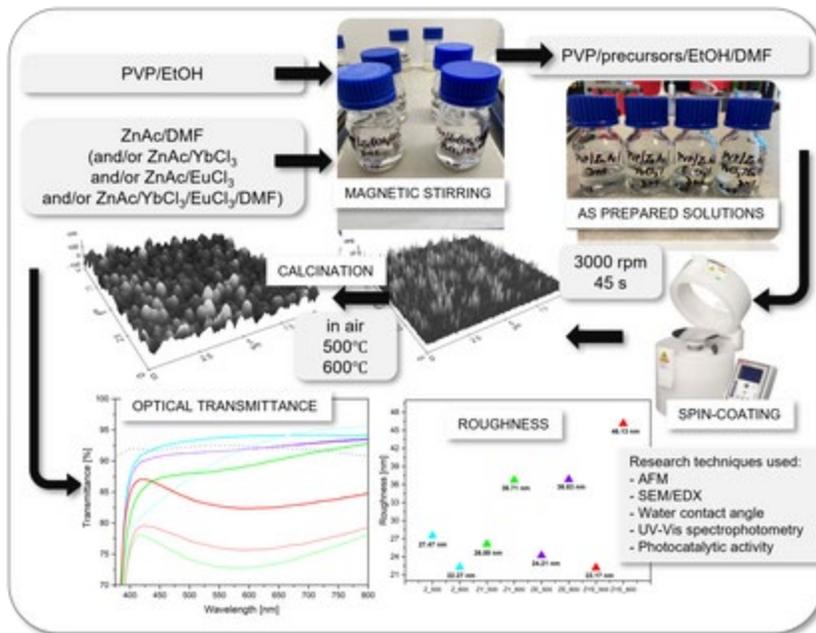
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Abstract

Utilization of the knowledge of the wettability of various surfaces and mimicking the effects of nature allows the production of cost-effective and uncomplicated self-cleaning coatings for advanced applications. Self-cleaning coatings use raindrops and sunlight in the cleaning process, which reduces manual cleaning and thus the maintenance costs of glass surfaces.

The most commonly used metal oxides, showing photocatalytic properties and appropriate wetting properties for their morphology of thin layers, are titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), vanadium oxide (V_2O_5) and tungsten oxide (WO_3). Among the materials mentioned below, TiO_2 is most popular in self-cleaning coating applications due to its exceptional photocatalytic and superhydrophilic properties. The second important oxide in self-cleaning coating applications is zinc oxide, which exhibits a chemical surface cleaning mechanism similar to TiO_2 using a photocatalysis process. A noteworthy property of both materials is superhydrophilicity obtained under the influence of ultraviolet radiation, which allows for a more efficient process of cleaning surfaces with ZnO or TiO_2 coatings.

Thus, the aim of this paper is to manufacture hybrid coatings in the form of pure ZnO and rare earth metal oxides doped ZnO thin films and further the investigation of wettability, thickness, roughness, optical transmittance, optical band gap and photocatalytic activity of the obtained materials. Yb_2O_3 and Eu_2O_3 are used as dopants to ZnO due to their outstanding optical properties and so far their harness in optoelectronic industry. In order to produce efficient self-cleaning coatings, the potential of sol-gel technique and spin-coating method is proposed, followed by annealing in high temperatures (500 and 600°C).



The obtained results indicate that undoped and ZnO- doped RE metal oxides thin films have a great potential in use of self-cleaning coatings on photovoltaic cells and glass constructions in architecture.

Keywords

self-cleaning coatings, photocatalysis, metal oxide thin films, rare earth metal oxides

P1.14

Fabrication of cotton fabric based strain sensor using polylactic acid/ graphene emulsion conductive ink

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Abstract

Nowadays, acquiring durable and reproducible electronics based on biodegradable and bio-based materials is demanded to confront electronic waste consequences. However, developing such sustainable materials with high conductivity remains a challenging task. Apart from this, in many cases, the use of toxic solvents may be unavoidable. Thus, a novel and efficient method formed on aqueous emulsion-based printable conductive ink sprayed on cotton fabric is evolved, which shows the feasibility of being used as fabric stretch sensors. Moreover, the influence of stretchability on the conductivity of the fabric-based sensor is investigated, and it exhibits high stability in cyclic strain tests suitable for wearable electronics.

Polylactic acid (PLA) is used as a bio-based binder to prepare the emulsion ink, and graphene nanoplatelets are used as a conductive filler. Spray-coated cotton fabric shows an encouraging electrical conductivity of 34.5 S/m. An additional improvement in electrical conductivity of conductive cotton fabric is gained by hot pressing post-treatment. Additionally, the mechanical studies of the coated fabrics have been studied. The findings illustrate enhancement of the mechanical properties of the cotton fabrics by increasing Young's modulus values almost twice compared to pristine fabric. This eco-friendly composite ink can be used as a strain sensor for transforming specific electronic components into biodegradable versions.

Keywords

Green electronics, Bio-based coatings, Conductive emulsion ink, Polylactic acid

P1.15

Comparison of optical properties of thin PVP/ In_2O_3 and PVP/ In_2O_3 / SnO_2 films fabricated by various methods

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Abstract

The aim of this study was to prepare thin layers of PVP/ In_2O_3 and PVP/ In_2O_3 / SnO_2 by electrospinning and spin coating and to compare their optical properties. First, three wt.% PVP solutions were prepared. PVP: undoped (as reference), with the addition of 10 wt.% In_2O_3 nanoparticles, 10 wt.% In_2O_3 and SnO_2 nanoparticles. Then, a part of each solution was subjected to the electrospinning process, the remaining solution was used in the spin coating process. The analysis of the morphology and surface topography of the produced layers was performed using a scanning electron microscope. It was confirmed that the electrospinning process resulted in a nanofibrous layer with uniformly distributed nanoparticles inside and on the surface of the defect-free fibers with a diameter of 130 nm to 2 μm (Fig. 1). The films obtained in the spin coating process were continuous, without defects, with deposited nanoparticles in the form of agglomerates with a size of 100 nm to 1.9 μm (Fig. 1). Additionally, the composition and chemical structure were confirmed by spectroscopic analysis using the Energy-Dispersive X-ray Spectroscopy and the Fourier-Transform Infrared Spectroscopy. The optical properties of the manufactured thin films were analyzed using a UV-Vis spectrophotometer. Based on the recorded spectra, the energy gap of the layers was determined. It was shown that nanofibrous mats doped with nanoparticles were characterized by a much lower band gap than undoped fibers. A decrease in the energy gap was also observed for samples produced by the spin coating method. The produced materials can be used in the production of advanced flexible electronic devices, radiation shield, optical band gap tuners.

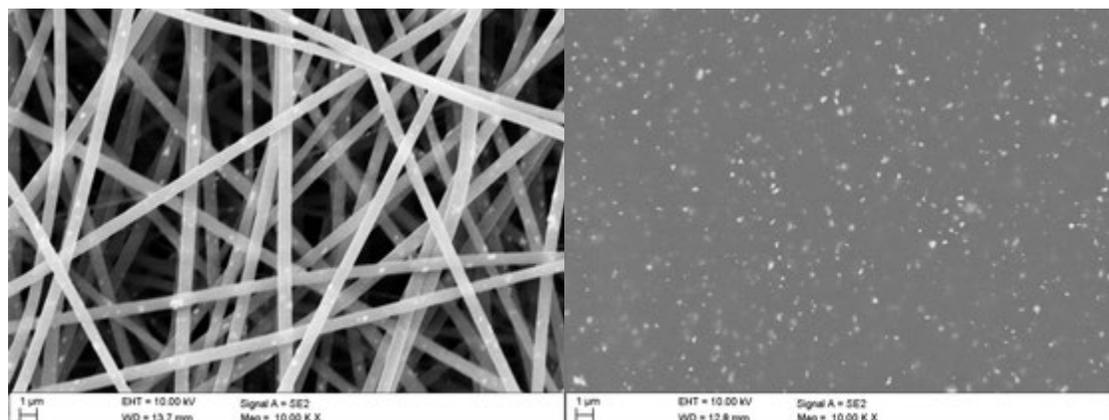


Fig. 1. Thin PVP/ In_2O_3 and PVP/ In_2O_3 / SnO_2 films

Keywords

thin films, electrospinning, spin coating, nanocomposite

P1.16

Patterning Gold Surfaces with Nitrophenylene Groups Based on Microcontact Printing and Electrografting

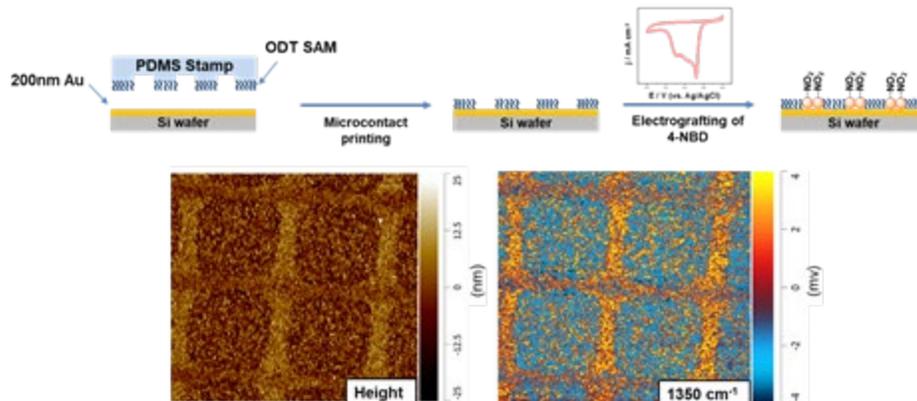
Jiangling Su, Guido Grundmeier

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Abstract

Developing the patterning surfaces for materials promoted as biological [1] and chemical sensors [2, 3] is still an important and ongoing research. Patterning self-assembled monolayers (SAMs) of alkane thiolates by microcontact printing (μ CP) is a commonly utilized technique for fabricating soft-lithography. However, patterning using electrografting of aryldiazonium salts is still a relatively novel endeavor.

In this work, patterning gold surfaces with nitrophenylene- and alkane-terminated functional groups were fabricated based on μ cp and electrografting. Here, we demonstrate two steps of the patterning procedure. Initially, a covalently transferred square pattern with alkanethiol functionalities was printed on gold surfaces using a μ CP with poly(dimethylsiloxane) (PDMS) stamp inked with an ethanolic solution of 1 mM 1-octadecanethiol (ODT). Subsequently, the electrografting of 4-nitrobenzenediazonium salts was performed by cyclic voltammetry (CV) for the formation of the grid pattern terminated with nitrophenylene. Surface morphology and topography images obtained by scanning electron microscopy (SEM) and atomic force microscopy (AFM) visually validate the pattern of the gold surfaces. The surface chemistry was investigated by means of polarization-modulated infrared reflection absorption spectroscopy (PM-IRRAS) and X-ray photoelectron spectroscopy (XPS). Furthermore, the result of nanoscale-Fourier transform infrared reflection (nano-FTIR) spectroscopy demonstrates the patterned regions terminated with nitrophenylene and alkane generating on the gold surface.



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Keywords

Electrografting, Microcontact printing, Patterning surface, Surface functionalization

P1.17

Comparative analysis of hexamethyldisiloxane and hexamethyldisilazane plasma polymer film structures before and after post-plasma oxidation

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Abstract

The surface functionalization of thin films by PE-CVD is of great interest for various applications, such as adhesive properties [1]. Hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSN) are typically employed for the deposition of thin functional films.

The goal of this presented work is to compare the structure and barrier properties of HMDSO and HMDSN plasma polymer films before and after plasma oxidation. For this purpose, an *in-situ* plasma set-up possessing the possibility to perform discrete polarization modulated-IRRAS (DPM-IRRAS) was used. This approach allowed for the IR characterization directly after plasma oxidation without the need to expose the surface to ill-defined ambient conditions. *Ex-situ* XPS was used to determine the change of the chemical structures in the surface near region. The film thickness and the refractive index were determined by ellipsometry. AFM illustrated the change in the surface morphology. Complementary, ToF-SIMS sputter profiling was performed to analyze the depth profile due to plasma conversion. The surface energies of the films were determined by the contact angle measurements. Finally, the barrier properties of the produced films were analyzed by means of EIS and could be well correlated with the structural information.

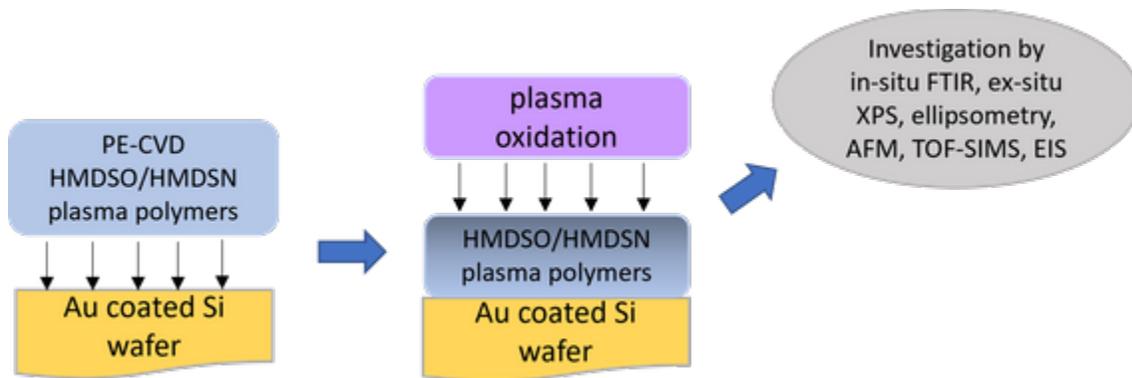
The results clearly show that the effect of the O₂ plasma treatment is the progressive removal of carbon from the films and the formation of Si-O bonds. Furthermore, the HMDSO and HMDSN deposited plasma polymer films have significantly different porous structures after post-plasma oxidation.

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Acknowledgments

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Keywords

plasma polymers, plasma oxidation, in-situ FTIR, surface functionalization

P1.18

Dual-curing urethane-methacrylate clearcoats: isocyanate blocked by methacrylate-functionalized pyrazoles with a benzophenone-containing polyol binder

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Abstract

Conventional thermally curable polyurethane-based automotive clearcoat systems have mainly consisted of a polyol binder and an isocyanate curing agent requiring toxic catalyst and high-temperature conditions. Research on lowering curing temperature without using catalysts has been a top priority for decades in the coating industry. Herein, we report a dual-curable clearcoat system that contains isocyanate curing agents blocked by methacrylate-functionalized pyrazole and a photo-initiative benzophenone containing polyol binder. Above 120 °C, blocked isocyanates can form a urethane bond with a polyol after deblocking and self-initiation of methacrylate can participate in the radical reaction. Furthermore, under UV irradiation, benzophenone can generate radicals which can further propagate methacrylate functional group as well as generate carbon-carbon bonds increasing overall crosslinking density. Rheological behaviors of the novel clearcoat systems were investigated by oscillatory rheometer under combined thermal and UV curing conditions. Also, surface mechanical properties of cured films prepared under three different curing conditions, (i) thermal, (ii) UV, (iii) thermal-UV, were compared which can relate to overall crosslinking density. This novel dual-curable, urethane-methacrylate clearcoats under thermal-UV curing process can not only contribute to enhancing surface hardness but also consuming unreacted methacrylate functional groups in the cured films.

Keywords

Dual-curable, Clearcoats, Pyrazole, Benzophenone

P1.19

Production of hydrogen with nano-sized carbon particles from cracking of liquid hydrocarbons using liquid-phase plasma

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Abstract

Hydrogen is firmly established as the clean energy of the future to alternative fossil fuels and solve serious climate change problems. Fuel cell technology is also rapidly advancing, and the era of power generation using hydrogen as an energy source is coming. In addition, as hydrogen vehicles to which fuel cells are applied are rapidly spreading, the importance of hydrogen energy is increasing. However, most of the current hydrogen production processes still rely on steam reforming of fossil fuels. This method has a fatal problem in that carbon dioxide is emitted during the production process. In this study, we propose a method for producing hydrogen from liquid hydrocarbons using plasma without generating CO₂. Liquid plasma has been used to directly crack liquid hydrocarbons at atmospheric pressure to produce hydrogen. Various catalysts have been applied to increase hydrogen production efficiency. The only gaseous product in this reaction was hydrogen and no CO₂ was produced. Simultaneously with hydrogen generation, nano-sized carbon particles without impurities were obtained as a solid product. The crystal size of the carbon particles was very small and uniform (10 nm or less). Liquid plasma cracked hydrocarbons to produce hydrogen and carbon, even in the absence of a catalyst. When the catalyst was applied to the hydrocarbon cracking reaction using liquid plasma, the rate of hydrogen generation was greatly increased.

Keywords

hydrogen Production, liquid-phase plasma, cracking of liquid hydrocarbon, nano-sized carbon particles

P1.20

Carbaryl electrodegradation using boron-doped ultrananocrystalline diamond /TiO₂ nanotubes composites

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Abstract

Carbaryl compounds are linked to environmental and health issues due to their ability to impair the proper functioning of the endocrine system. Widely used in agriculture, this chemical reaches the rivers where the electrochemical oxidation (EO) becomes an alternative to its tradition removal. This work presents new porous B-UNCD_{WS}/TDNT/Ti composites obtained without seeding (WS) pre-treatment applied as anodes to the Carbaryl electrodegradation. Titanium dioxide nanotubes (TDNT) have high chemical stability and large surface area, while boron-doped ultrananocrystalline diamond (B-UNCD) has a large electrochemical window, stability, and chemical inertia. Titanium sheets were anodized in an organic electrolyte under 60 V and 40°C for two times to obtain the TDNT substrate. After the 1st anodization, the initial layer of nanotubes was removed by tape followed by the 2nd anodization to increase the sample morphology organization. Then, the B-UNCD_{WS} films were grown on it during 7h without a seeding pre-treatment by hot filament chemical vapor deposition technique using a H₂/CH₄/Ar gas mixture. Doping was obtained from an additional H₂ line containing B₂O₃ dissolved in methanol. These materials were analyzed by SEM, Raman spectroscopy, X-Ray diffraction, and their surface area was also evaluated. Finally, the anodes were applied to Carbaryl removal, with total degradation in 40 min and almost total mineralization in 240 min. The main by-products were short-liner carboxylic acids such as oxalic, fumaric, formic, and acetic, while the initial N contained in the molecule was preferentially converted to ammonium. Therefore, the results proved that B-UNCD_{WS}/TDNT/Ti has great feasibility in removing the carbaryl from water.

Keywords

Electrodegradation , Carbaryl, Boron doped diamond, Titanium dioxide nanotubes

P1.21

BIOCHAR OF PYROLYSIS FROM FILTER MUD RESIDUE GENERATED IN INDUSTRIES OF SUGAR AND ALCOHOL

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Abstract

The study presents an alternative treatment with pyrolysis (380 °C) to filter sludge residues obtained in sugar and alcohol industries in Rio de Janeiro - Brazil and the main objective was to generate the biochar to be applied in the adsorption process of the thiamethoxam pesticide in wastewater. The biochar was featured based on moisture, volatile matter, ash content, surface area, porosity, elemental analysis, fourier transform infrared spectroscopy, and scanning electron microscopy. The characterization indicated that biochar is promising for the removal of organic compounds by the adsorption process due to its surface area ($19.8 \text{ m}^2 \text{ g}^{-1}$), mesoporosity and functional groups such as hydroxyl present on the surface of the biochar. The biochar adsorption capability was investigated for the removal of thiamethoxam in aqueous solutions. Langmuir and Freundlich models of adsorption isotherms were studied. The pseudo-first and pseudo-second order models were used in the kinetic study of the adsorption process. The results shown that after 30 min there was a removal around 70 % of thiamethoxam from aqueous solution at a concentration of 10 mg L^{-1} . In addition, adsorption process was well described by the Langmuir isotherm and pseudo-second order models. Then, the biochar from filter mud can be alternative for treatment of wastewater contaminated with thiamethoxam.

Keywords

Biochar, Pyrolysis, Adsorption, Pesticide

P1.22

Density functional theory study of dacarbazine adsorption on functionalized carbon surface

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Abstract

One strategy proposed to modulate the undesired effects of a drug is designing new carriers with promising and improved pharmacological profiles through the application of carbon surface chemistry. The carbon skeleton could play the fundamental role of a carrier with improved therapeutic efficacy mainly via the functionalization of its surface. In doing this, we propose an activated carbon surface as a carrier of dacarbazine drug that can potentially signify an outstanding candidate for further pharmaceutical development. Vienna Ab initio Simulation Package based on Density Functional Theory can supply important aspects by providing atomistic details through molecular modeling.

The overall weak interactions between dacarbazine and pristine carbon surface could limit therapeutic treatment efficiency. In contrast, the presence of the carboxyl functional group on carbon surface has an important effect on the adsorption of dacarbazine at neutral and low pH. When the surface is functionalized, the molecule is adsorbed more strongly compared to the adsorption on pristine carbon surface. Changes in pH can cause a deprotonation/protonation of amine and $-\text{COOH}$ functional groups leading to a change in the charge of the molecule/surface groups. Accordingly, at low pH, the protonated dacarbazine is attracted by the carboxyl-carbon surface via H-bonding and electrostatic interactions, which result in the lowest adsorption energy (the most stable). At pH=7, the decreased electrostatic interactions between the neutral molecule and the functionalized surface cause an increase in the adsorption energy. Finally, at high pH, the strong electrostatic repulsion between the deprotonated drug and the ionized ($-\text{COO}^-$) carboxyl group results in the highest dacarbazine adsorption energy on the functionalized carbon surface.

Carbon materials are acquiring a growing number of applications. The function is established by their texture and surface chemistry. Carboxyl-functionalized carbon surfaces could improve dacarbazine drug delivery adapting to therapy requirements according to pH.

Keywords

DFT, carbon, dacarbazine, drug delivery

P1.23

Ethanol adsorption on Ni doped Mo₂C(001): A DFT study

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Abstract

Ethanol adsorption on Ni/Mo₂C (001) surface at low coverage is studied using density functional theory calculations (with van der Waals corrections). The Mo₂C surface is modeled from the hexagonal closed-packed (hcp) phase carbide (b-Mo₂C). We considered the Mo termination and a single Ni as an adatom. The most favorable location for Ni was a fcc site and some charge is transferred from the surface to this atom. Ethanol is then adsorbed on top of this Ni site with -1.47 eV. The electronic structure (DOS) of Mo₂C present a metallic character and Ni a narrow d band shifted above the Fermi level by the carbide influence. The DOS of ethanol based states are stabilized to lower energies. The most affected are those states from -OH group. A bond is formed between Ni-O(Ethanol) while the -OH distance shows an elongation of only 1.7 %.

Keywords

DFT, Ethanol, Mo₂C, carbide

P1.24

Low-cost mass producible nanostructured surface on flexible substrate with ultra-thin gold or silver films for SERS applications

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Abstract

In recent years Surface-Enhanced Raman Scattering (SERS) has emerged as a powerful analytical technique. The ultra-high sensitivity combined with fingerprinting recognition capabilities of SERS enables trace level detection of the analytes [\[i\]](#), [\[ii\]](#). The SERS effect is mainly explained with the, “localized surface plasmon resonances” and the “chemical” or “charge-transfer” mechanisms [\[iii\]](#)

To extend the use of SERS in real life applications, there is a need to develop low-cost environment-friendly disposable analysis chips to ensure high accuracy and avoid the risks of cross contamination. Existing methods have limitations in terms of throughput volume and/or cost [\[iv\]](#). Furthermore, one of the challenges with mass producible SERS-active nanostructures is the reproducibility of the signal intensity.

Paper is a low-cost, flexible and environment-friendly substrate. Proof of concepts for paper-based printed electronics [\[v\]](#), [\[vi\]](#) and platforms for analytical applications have been reported in the literature [\[vii\]](#), [\[viii\]](#). However, for SERS, paper is not an ideal substrate as it can create background disturbance. Here we report SERS-active nanostructured-paper substrate without background disturbance with ultra-thin (as low as 2nm) gold or silver layer. SERS-active substrates were tested with probe molecules (rhodamine 6G and crystal violet). High sensitivity and good spatial reproducibility is achieved.

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[\[viii\]](#) A. Määttä et al., Sensors and Actuators B: Chemical, 177 (2013) 153-162.

Keywords

SERS, nanostructure, gold, silver

P1.25

Formation of antibacterial coating on titanium dental implant for animal

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Abstract

Titanium dental implants are widely used in veterinary medicine. For animals, time of osseointegration process is important, due to low restrictions of animal mobility. It is difficult to control animal to avoid septic inflammations. Thus, antibacterial properties of the long-term implant are desirable.

Titanium dental implant surface could be modify via plasma electrolytic oxidation process. On implant surface a porous oxide layer is formed with incorporated chemical compounds e.g. calcium, phosphorous. However, during this process a sensitive antibacterial compound could not be effectively incorporated.

In this work, we present a formation a hybrid oxide-polymer layer, composed of poly(sebacic anhydride) and amoxicillin. Dental implant was anodized in 0.1M Ca(H₂PO₂)₂ solution at 350V. Porous oxide layer was composed of Ca and P compounds. We have found, that 1% w/v solution of polymer in chloroform is optimal to form a polymer layer with loaded amoxicillin, on anodized surface of dental implant. Depending on immersion speed of anodized implant in polymer solution with drug, concentration of loaded amoxicillin varied. After 1h of dental implant immersion in PBS solution, concentration of drug released from coating was between 1.87 mg/mL–3.61 mg/mL. Concentration of amoxicillin released from the surface increased over time. Concentration of amoxicillin was enough to obtain inhibition zone for reference bacteria strain *Staphylococcus epidermidis* (ATCC12228). Extract collected of from the dental implants was cytocompatible with fibroblast L929 and osteoblast-like MG-63 cells. Viability of the investigated cells was more than in 70% after 24h of culture.

Formation a functional coating on dental implant may find application in veterinary, and protect surface against formation bacteria biofilm.

Acknowledgments

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Keywords

titanium implant, bioactive, antibacterial, coatings

P1.26

New Hybrid 2D TiO₂-PEDOT Composites – the Influence of Polymer Morphology on Cr(VI) Photoreduction under Simulated Solar Irradiation

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Abstract

The present study represents an innovative approach to developing organic-inorganic hybrid materials that can be used for photocatalytic removal of heavy metals from the aqueous environment. The composite of titanium(IV) oxide and poly(3,4-ethylenedioxythiophene) (PEDOT) of different morphology was obtained and applied for hexavalent chromium removal from the aqueous phase in the presence of simulated solar light.

At the sixth oxidation state, chromium can be used as an anti-corrosion agent added to paints, primers, and other surface coatings. However, Cr(VI) shows adverse effects on the environment because of its carcinogenicity, toxicity, and high aqueous solubility properties. Nevertheless, it can be reduced to chromium(III), which is 1000-times less cytotoxic to cultured diploid human fibroblasts, additionally can be easily precipitated and removed.

Several methods have been developed to remove Cr(VI) from aqueous solutions, including ion exchange, chemical precipitation, adsorption, and membrane separation techniques. Photocatalysis has been proposed as a green technology for removing toxic and emerging contaminants.

The synthesis of PEDOT proceeded in a w/o microemulsion system in an oxidative polymerization reaction, which enabled obtaining different polymers' structures. The obtained hybrid photocatalysts were characterized by diffuse reflectance spectroscopy, infrared spectroscopy, X-ray diffraction, microscopic analysis, specific surface analysis, cyclic voltamperometry.

Four structures were identified: (I) globular, (II) consisting of spherical particles and folded plates, (III) sticky, elongated structures, (IV) microvesicular. Photocatalytic Cr(VI) reduction under simulated solar irradiation indicated the highest photocatalytic activity of 2D TiO₂-PEDOT composites with microvesicular morphology. All modified samples were characterized by low adsorption of Cr(VI). The synergistic effect of 2D TiO₂ and PEDOT for Cr(VI) removal was observed in UV-Vis light, which resulted from the increased separation of photogenerated electrons and holes involved in redox reactions.

Acknowledgments

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Keywords

Cr(VI) reduction, PEDOT, photocatalysis, TiO₂

P1.27

The investigation of thermal and optical properties of semiconducting polymers blends

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Abstract

In this paper Authors focused on investigation of the thermal and physical properties of polymeric thin films based on semiconducting polymers mixtures. Materials selected for the research were PDPP4T (Poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione -3,6-diyl)-alt-(2,2';5',2'';5'',2'''-quaterthiophen-5,5'''-diyl)] and DPPDPyBT (Poly(2,5-bis(2-octyldodecyl)-3,6-di(pyridin-2-yl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-2,2' bithiophene). The materials were selected for their electrical properties (i.e. narrow optical band gap, high charge-carrier mobility) enabling them to be produced from their mixtures volumetric (bulk) p-n heterojunction.

The article describes the influence of the mutual participation of materials on the structure and optical transmission and glass transition temperature of blends.

In order to analyze the structure, optical and thermal properties of the obtained layers transmission, variable-angle and variable temperature spectroscopic ellipsometry, X-ray diffractometry, DSC and scanning electron microscopy were used. The measurements (except of temperature-dependent ellipsometry and DSC) have been taken before and after annealing.

The ellipsometric measurements have been conducted with use spectroscopic ellipsometer, which operates in the spectral range of 240–2500 nm. The research in transmission mode were performed in all UV–Vis/NIR spectral range. The measurements of ellipsometric angles Ψ and Δ were performed for incidence angle 40°–70° range with the 5° step. The transmission mode has been utilized for measurement of the optical transmission, the variable angle mode for determination of the thickness and variable-temperature mode for determination the glass transition temperatures) T_g. The results of ellipsometric and differential scanning calorimetry tests confirms the influence the mixtures composition on the optical transmission and glass transition temperature. X-ray studies showed that the heat treatment of the influenced the morphology of polymer samples.

Keywords

organic semiconductors, ellipsometry, thermal properties, optical properties

P1.28

Effect of surface modification of Ti-SBA-15 catalyst on the course of epoxidation of 1,5,9-cyclododecatriene with hydrogen peroxide

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Abstract

The subject of these studies is the effect of surface modification of Ti-SBA-15 catalyst (with the Si:Ti molar ratio in crystallization gel equal to 30:1) on the results of epoxidation of 1,5,9-cyclododecatriene (CDT) with the aqueous solution of H₂O₂ used as the oxidant. The catalyst was modified by trimethylsilylation of the surface hydroxyl groups to increase the hydrophobic properties of this porous material. To the best of our knowledge, there are no literature reports on the use of modified in this way Ti-SBA-15 material in the process of CDT epoxidation. According to our hypothesis, the hydrophobization of the surface of the catalyst should facilitate the contact of the CDT molecule with the catalyst surface, while hindering water access and hydrolysis of the epoxy bond. Trimethylsilylation of Ti-SBA-15 was performed with hexamethyldisilazane, which selectively reacts with surface -OH groups.

Preliminary studies were carried out under the following process parameters: concentration of a solvent - isopropanol (i-PrOH) 80 wt%; CDT:H₂O₂ molar ratio 2:1; H₂O₂ concentration 60 wt%; temperature 70°C, and reaction time 4 h. The conducted studies showed that trimethylsilylation reduces the rate of the epoxidation reaction (the conversion of CDT after 4 h of reaction carrying out for unmodified Ti-SBA-15 reaches value 15 mol% and for modified Ti-SBA-15 it amounts to 11 mol%) and slightly enhances conversion of H₂O₂ (after 4 h for unmodified Ti-SBA-15 it amounts to 66 mol% and for modified Ti-SBA-15 is equal to 74 mol%). While we anticipated a reduction in the reaction rate due to the hindered contact of H₂O₂ with the catalyst surface, its higher conversion was a surprise to us.

Further studies presented at the conference will more closely examine the effects of process parameters (temperature, solvent type, and CDT:H₂O₂ molar ratio) on the course of the examined process.

Keywords

Ti-SBA-15, catalyst, oxidation, hydrophobicity

P1.29

High performance supercapacitors using selenium partially reduced Co₃O₄@ carbon cloth electrode with 3D interconnected architecture nanowires

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Abstract

The electrodes with large specific surface area, appropriate pore size distribution and high electric conductivity are highly desirable for supercapacitors applications. Herein, we utilized a hydrothermal and consequent annealing approach to fabricate 3D interconnected architecture nanowires of selenium partially reduced spinel Co₃O₄ grew on the carbon cloth (COS@CC). The binder-free COS@CC electrode exhibits high specific capacitance, 2039.9 F g⁻¹ at 1 A g⁻¹, excellent rate capability, 51.6% capacitance retention and superior cyclic stability, 92.0% retention of initial value up to 15000 cycles. These electrochemical performances were found to be better than that of Co₃O₄@CC electrode. The enhanced electrochemical performance may be attributed to the fact that the 3D interconnected architecture nanowires could shorten the ion transfer distance and increase the rate of the electrochemical reaction. In addition, the increased specific surface area and homogeneous mesopore size distribution of the electrode could assist effective diffusion and transfer of OH⁻ between electrode and electrolyte. The enhanced electrical conductivity of the electrode, which is caused by the selenium partial reduction, facilitates electron transports and consequently improves the electrochemical properties of supercapacitors. These remarkable electrochemical performances display the COS@CC can be used for the high energy and power density supercapacitors.

Keywords

3D interconnected architecture nanowires, selenium partially reduced, spinel Co₃O₄, binder-free

P1.30

Electronic and magnetic properties of TiO₂@Fe₂O₃ nanostructures for photocatalytic application.

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Abstract

The unique optical, magnetic, electrical, and photocatalytic properties of TiO₂ nanocrystals are widely used in many fields such as solar cells, gas sensors, photocatalysis, air purification, and coatings. In addition to these features, TiO₂ NCs are also non-toxic, highly stable, and show high UV absorption.

After combination with a metal oxide, the photocatalytic properties of titanium dioxide can be improved e.g. by covering with Fe₂O₃ nanoparticles to form a heterojunction. It is necessary because the band gap of TiO₂ is equal to 3.2 eV and the absorption of sunlight energy is relatively low. However, by compounding with Fe₂O₃ with a 2.2 eV band gap, the absorption range is extended to visible light.

The aim of this work is to study the electronic and magnetic properties of the TiO₂@Fe₂O₃ heterojunction and the crystal structure of the Fe₂O₃ at the surface. The precipitation method was used to obtain nanostructures with different amounts of Fe₂O₃. As a result of the deposition process, the incorporation of Fe³⁺ ions into the TiO₂ lattice was confirmed by the XPS study, and further, the oxidation state of iron was verified by Mössbauer spectroscopy. The magnetic measurements allowed to investigate the future possibilities of photocatalyst separation from a reaction medium with the help of an external magnetic field.

The comprehensive study of the TiO₂@Fe₂O₃ heterojunction is expected to lay a good foundation for further research in the field of photocatalysis. The XRD, SEM, XPS, magnetization measurements, UV-vis, and Mössbauer Spectroscopy were used to characterize obtained materials.

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Keywords

TiO₂@Fe₂O₃ heterojunction, TiO₂:Fe layer, oxidation state, oxygen vacancy

P1.31

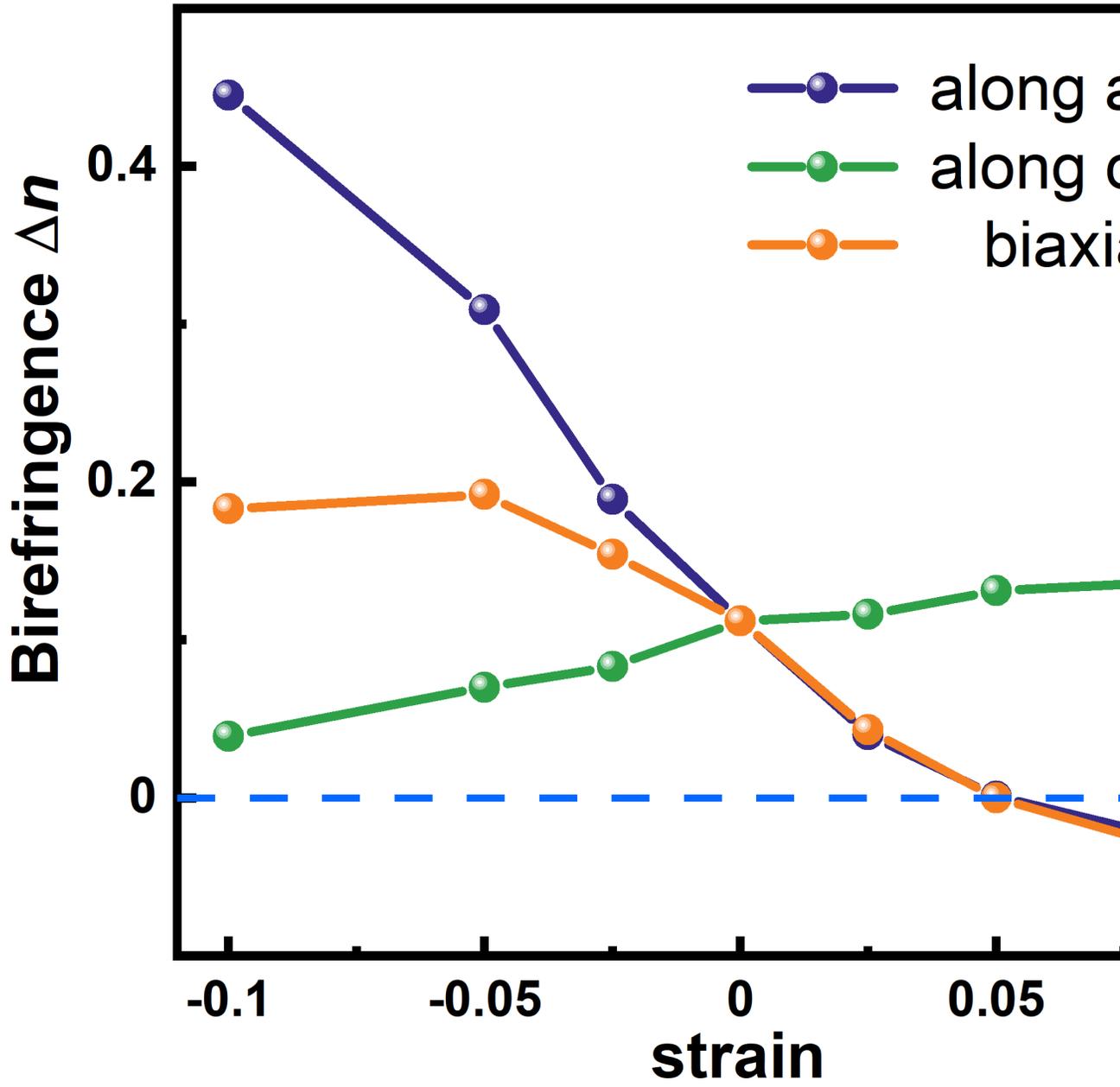
Highly tunable optical property of α -MoO₃ by strain engineering: from isotropy to giant improvement of anisotropy

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Abstract

Strain engineering offers a great opportunity to tune optical properties of materials [Appl. Phys. Rev. 8, 021318 (2021); InfoMat 3.4 (2021): 397-420.]. However, there is scarcely report about tuning the optical properties of α -MoO₃ by strain engineering as far as we know. Using first-principle calculations, we find that by applying in-plane strain the optical property of α -MoO₃ can be tuned with giant improvement of anisotropy and even be isotropy for strain along a -axis and biaxial strain. The quantitative index of optical anisotropy is the birefringence, shown in the figure below.



Keywords

optical anisotropy, strain engineering, α -MoO₃, first-principle calculations

P1.32

Change in the energy storage mechanism of NiO/RGO/CF electrodes

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Abstract

Energy storage devices such as batteries, capacitors and supercapacitors are responsible for an important part of human evolution and have been used in our daily lives for a long time. Thus, the demand for energy storage devices with greater energy storage capacities has generated a considerable increase in interest in the development of materials used as electrodes in batteries and supercapacitors - SC. In the most cases, the energy storage mechanism of an electrode is determined by the material used in its composition. Thus, materials that store energy through faradaic reactions are applied in batteries, while materials that store energy through non-faradaic ways are used in SC. In this work, it was observed that, after a careful adjustment of the calcination temperature, the NiO/RGO/CF ternary composite presented an impressive change in the energy storage mechanism. It was found after the electrochemical analysis that ternary composite treated at 300°C had a characteristic behavior of battery-type materials, but the same material treated at 500°C presented supercapacitive properties. To obtain ternary composites, firstly the CF samples were submitted to the chemical oxidation process using nitric acid 60% (v/v) at 110 °C under reflux for 30 min. GO was deposited on the CF by a dip coating method and then it was reduced using the thermal method at 1000°C for 1h. Then, the RGO/CF binary composite was kept in a hydrothermal reactor containing Ni(NO₃)₂ aqueous solution for 3h at 200°C. Finally, the ternary composites were calcined for 5h at temperatures of 300, 400, and 500°C. The ternary composites were characterized by scanning electron microscopy, Raman spectroscopy, and X-ray diffraction. The electrochemical analyses performed after calcination at 500°C showed that the electrodes completely changed the energy storage mechanism. This behavior has been described very few times in the literature, highlighting these attractive results.

Keywords

Supercapacitors, Batteries, Energy storage, Composites

P1.33

Development of a biobased and conductive ink to functionalize stretchable surfaces for robotic applications

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Abstract

A biobased ink that contains a biobased polymer and a biobased plasticizer, which is added to increase the stretchability, the flexibility and the dissolution of the biobased polymer in two biobased solvents has been designed. Graphene nanoplatelets have been added to the ink to make it conductive. The well-dispersion of all the components has been validated by SEM analysis. The ink aim is to functionalize several substrates, such as nitrile rubber. To improve the adhesion, a pre and post-treatment is conducted on the specimens: before the application of the conductive ink by spray coating, a solution of acetic acid is applied with a pipette on the nitrile rubber surface [1], after the ink application the composite is hot pressed to ensure a good adhesion and spreading of the ink on the surface. One of the possible application for this composite material is the use in biomedical electronics or humanoid and soft robotics that do not required high level of deformation [2,3]. Then, the convenience of the ink on the surface has been tested through 50 cycles of loading-unloading stretching tests up to 30% of deformation. It has been found that the composite material can be deformed up to this level while still being conductive.

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Keywords

biobased ink, graphene, adhesion, robotics

P1.34

Vinyl acetate-vinyl laurate copolymer and curcumin coatings with reduced bacterial adhesion and antioxidant properties

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Abstract

Poly(vinyl acetate)-vinyl laurate copolymer and curcumin are implied to make functional coatings. The copolymer is commercially developed as biodegradable chewing gum base, whereas curcumin is a well-known natural compound used mainly for its strong antioxidant activity. Coatings are applied on glass but also on natural alginate and gelatin free standing film by using the dip coating technique. Coatings remain transparent in the visible range conferring UV filtering properties. In addition, the flexibility is maintained when applied on the natural films. Furthermore, the biocompatibility of the coating is demonstrated by cell proliferation and the low bacterial adhesion properties are confirmed by bacterial surface contamination experiments. This sustainable coating could be a viable option for giving antioxidant and bacterial resistance properties to natural polymeric films that might be used for food packaging or other relevant applications.

Keywords

vinyl acetate-vinyl laurate, UV-blocking, antioxidant, coating

P1.35

Growing of FePO₄/LiFePO₄ conversion layer on iron sheets

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Abstract

Energy production based on coal, oil, and gas is the main responsible for climate change. Thus, Governments' activity focuses on increasing the fraction of renewable energy employed in vehicles by boosting the use of electric vehicles. Li-ion batteries represent nowadays the reference energy storage system to decrease the dependence on fossil resources. In this sense, LiFePO₄ (LFP) based batteries represent an appropriate technology for the automotive industry. LFP is a non-toxic cathode, low cost, safe, and highly reversible.

The cathode material and the electrical contact between the active material and the current collector still represent the main limitation for the cell capacity increase. The present work is devoted to the direct growing of LFP layers on Fe⁰ sheets by electrochemical synthesis. Being the iron sheet the current collector, a high conductivity at the iron/phosphate active material interface seems guaranteed. The conversion layer was created by the cyclic voltammetry technique. H₃PO₄ and LiOH in different concentrations were used as electrolytes.

The electrolyte conductivity, pH, and concentration are key parameters in the final morphology and properties of the conversion layer. The best results were obtained at pH 4 and conductivity between 32-37 mS/cm. Films formed with the optimised electrolyte parameters showed high adherence and porosity.

The conversion layers were synthesized by cyclic voltammetry, between -0.7 V and 1.4 V vs. SCE. Different scan rates and an increasing number of cycles were tested to study the effect on the thickness and morphology of the grown layers.

Scanning Electron Microscopy (SEM) was used for the morphological characterization. The chemical characterization was performed by Electrochemical Impedance Spectroscopy (EIS), Energy Dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD).

Keywords

Li-ion batteries, Lithium iron phosphate, EIS, SEM

P1.36

Investigation of the interfacial self-healing properties of polycaprolactone coated glass fibers/epoxy composites

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Abstract

In fiber-reinforced polymer composites, the interphase between the matrix and the fibers dictates the properties of the final component. After a damage event, a self-healing interphase is able to fully or partially restore the interaction between the two phases if subjected to external stimuli, for example to heat. The healing process extends the service life of the composites, reducing the waste and the repairing costs, therefore improving the sustainability. This work is focused on the investigation of an innovative application for Polycaprolactone (PCL) that is reduced to nanoparticles dispersed in water solutions to coat the glass fibers surface and to create a self-healable interphase for polymer composite applications. The glass fibers were provided both with and without the typical superficial sizing to investigate the effect of the sizing with the deposited nanomaterial. The morphological observation of the coating was performed by Scanning Electron Microscopy (FESEM) and an example is reported in Figure 1. Increasing the solutions concentration and the applied voltage during the EPD process, the amount of deposited nanoparticles on the glass fibers increased. The healing of the interphase was induced by heating micro-composites that were prepared by depositing a single micro-drop of an epoxy resin on the coated fibers. From the micro-debonding tests, the healing efficiency ($HE_{\%}$) was calculated as the ratio between the interfacial shear strength (IFSS) after and before the healing process. Interesting results were obtained and compared for both types of fibers, showing a recovery of the IFSS of about 50% than the initial fiber/matrix interphase.

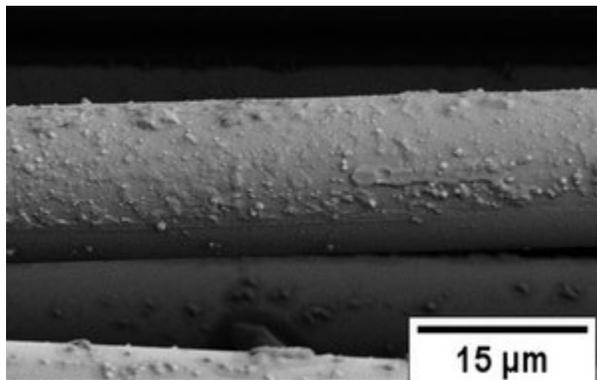


Figure 1. Example of a Polycaprolactone (PCL) coated glass fiber.

Keywords

self-healing, coating, Polycaprolactone, interphase

P1.37

The effect of cellulose nanofibrils and SWCNT dispersing agent on thermal and electrical conductive properties of hybridized flexible thin films

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Abstract

Nanocelluloses (NC) have been studied as high technology biopolymers for application in various materials, including the development of films or coatings and reinforcement of an e.g. paper. NC has been also studied as an efficient dispersing agent for Carbon Nanotubes (CNT), resulting to a thermally stable, mechanically strong and electrically conductive composite, generating new and forthcoming niche applications in e.g. transportation (electrification of vehicles), telecommunication (optical interconnects), consumer devices (high-density packaging / paper / films with smart / functional / digitalized properties for electronics, wearable materials etc.).

Thermally stable and electrically conductive materials combine exceptional mechanical, thermal and electrical conductive properties with strong electromagnetic (EMI) shielding and good heat transfer to be used for an electronic applications. The aim of this work was thus to identify the effect of different types of cellulose fibrils (phosphorylated and native cellulose nanofibrils / PCNF and CNF vs. cellulose microfibrils / MFC) and the addition of differently pre-dispersed Single-Wall CNT (SWCNT) on structural (SEM, density/porosity), surface wetting (contact angle), thermal (TGA/DSC), mechanical (tensile strength) and electrical conductive properties of thin films prepared by solvent-casting method.

Acknowledgement. This work was financially supported by the Slovenia Research Agency (grant No. J2-3053).

Keywords

Nanocellulose, Single-wall CNT, Thin film, Conductivity

P1.38

Curcumin-loaded PCL highly porous composites for rapid amine gas detection

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Abstract

In the field of colorimetric indicators, several challenges still need to be tackled, such as their detection limit and real-time monitoring capability. Most of the existing food spoilage indicators are fabricated in the form of films, something that cannot give them the accuracy needed, due to lack of porosity and low surface to volume ratio. Furthermore, the evaluation of their pH-induced color changes is done either only with liquid buffer solutions or with food demo tests, whereas tests with amine vapors produced during spoilage are scarcely reported. These can lead to false estimations of the food quality and therefore, the consumption of spoiled food.

To overcome these challenges, fibrous materials have been fabricated for use as pH indicators in food applications. These materials present high active surface area that allows their better interaction with various substances, and thus, their faster response with respect to films. However, the responsive capability of such materials can be adjusted not only by the porosity induced by the fibers, but also by the existence of pores on each fiber, which further enhance their active surface area.

Hence, curcumin-loaded polymeric porous fibrous mats were fabricated by non-solvent induced phase separation electrospinning for use as colorimetric indicators for the rapid detection of amine vapors. Their color change capacity was explored and compared to the one of their non-porous equivalents. Indeed, the ultra-porous system presented significantly higher surface area and consequently higher responsivity to dimethylamine vapors, showing a distinct color change within the first seconds of exposure, even in the presence of very low vapor concentrations. CIELab analysis demonstrated that the differences between the initial and the final color of the indicator after interaction with amine vapors are visually perceivable and reversible, enabling its use for several times, making it a sustainable colorimetric indicator system for smart packaging.

Keywords

Porous electrospun fibers, Gas sensing, pH indicator, Intelligent packaging

P1.39

IR-spectroscopic perspective on degradation of functional layers in perovskite solar cells

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Abstract

Perovskite photovoltaics is considered to be one of the most promising technologies for efficient conversion of solar energy into electricity [1,2]. The main limitation hindering a wider use of this technology is the relatively poor environmental stability caused by various degradation factors [3,4]. A number of characterization techniques have been employed for the study of degradation in perovskite devices [5,6,7]. Herein we focus on application of infrared spectroscopy to monitor degradation and accompanying evolution of the molecular structure in individual functional layers, as well as their combinations. In spite of its high sensitivity, non-invasiveness and relative simplicity, the use of IR spectroscopy to the study of degradation in perovskite solar cells has been rather limited. This work studies the evolution of the chemical structure of separate functional layers and their combinations under the influence of ambient atmosphere and temperature focusing on the range of characteristic vibrational features 370-7800 cm^{-1} and in a wide temperature interval from 170K to 370K. On the basis of IR spectroscopy, we aim to identify the specific routes and rates of degradation of the individual solar cell layers, as well as characteristic activation energies of processes underlying degradation. The materials used as individual functional layers are characterized by different chemical nature and morphology with TiO_2 and Spiro-OMETAD selected as, respectively, the archetypal electron- and hole-transporting layers, and $\text{CH}_3\text{NH}_3\text{PbCl}_3$ as the representative perovskite material. The IR measurements are complemented by optical and electrical studies and numerical simulations to build a comprehensive model of device degradation. Based on the results of the study, this approach is applied to other photovoltaic systems, including lead-based perovskite solar cells. It is hoped that the presented results will help further enhance the performance and stability of materials and devices under atmospheric conditions on the route to creating stable and sustainable perovskite photovoltaics.

Keywords

IR spectroscopy , Perovskite, Photovoltaics, thin films

P1.40

Electrochemical and surface properties of Zn phosphate layers: pickling, activation and bath composition

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Abstract

Zinc phosphate coatings are used in many sectors of industry, from the automotive to construction, due to characteristics as corrosion protection or lubrication effect. This work aims to investigate the properties of zinc phosphate layers deposited on high-strength steel under different operating conditions. The modification of three stages in the phosphating process is studied. Thus, the pickling acid, the activation stage prior to the phosphating bath, and the phosphating bath itself was modified in order to assess their influence on the phosphate layer efficiency.

With the purpose of replacing the harmful sulphuric acid commonly used in the pre-cleaning stage, a less risky acid, in particular, citric acid, was considered. The influence of the activation prior to the development of the layer was also evaluated. Thus, layers growth with and without the activation has been analysed. Finally, the addition of graphene oxide in the phosphating bath was examined. The properties of the phosphate layers obtained with and without the additive were compared.

Electrochemical techniques, such as Linear Sweep Polarization (LSV) and Electrochemical Impedance Spectroscopy (EIS), were employed to evaluate the corrosion resistance of the prepared phosphating layers. In addition, EIS data allowed obtaining other characteristics of the films as the resistivity and the porous structure. The study was completed by surface analysis with Scanning Electron Microscopy (SEM-EDX) to characterize the morphological and chemical structure of the obtained layers. Wear mass loss and wear coefficient were also assessed by Pin on Disk tests under controlled temperature and humidity conditions.

Keywords

phosphate, corrosion, impedance, SEM

P1.41

TRIBOELECTRIFICATION TECHNOLOGY FOR GRAPHENE COATINGS ON GLASS FIBERS

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Abstract

In this work a novel nanomaterial deposition method based on the triboelectrification effect, i.e the electrification of materials induced by their physical contact, was investigated. A lab-made setup was built to allow continuous glass fibers to be triboelectrified by Polytetrafluoroethylene (PTFE), in order to induce a positive electrification on their surface that attracted negatively charged graphene oxide (GO) nanosheets dispersed in water solution. The coated fibers were subsequently chemically reduced and used together with a bicomponent epoxy matrix to obtain single-fiber microcomposites. In order to study the effectiveness of the deposition method, a morphological observation of the coated fibers was carried out by field emission scanning electron microscopy (FESEM), which revealed a high quality and homogeneity of the coating with an increase in the deposition as the GO solution concentration increased. The same increment was not seen by increasing the intensity of the triboelectrification. The fiber/matrix interfacial shear strength was evaluated by microdebonding tests that revealed an improvement in the fiber/matrix adhesion up to 45% compared to the uncoated fibers. The electrical conductivity of the reduced graphene oxide (rGO) coated fibers was measured by a four-point probe and estimated around $10 \Omega \cdot m$, showing an increase with respect to pristine fibers.

Keywords

Glass fibers, Graphene, Triboelectrification, Interfacial adhesion

P1.42

Investigation of grain growth induced strains in BaCeO₃ films formed by e-beam vapor deposition

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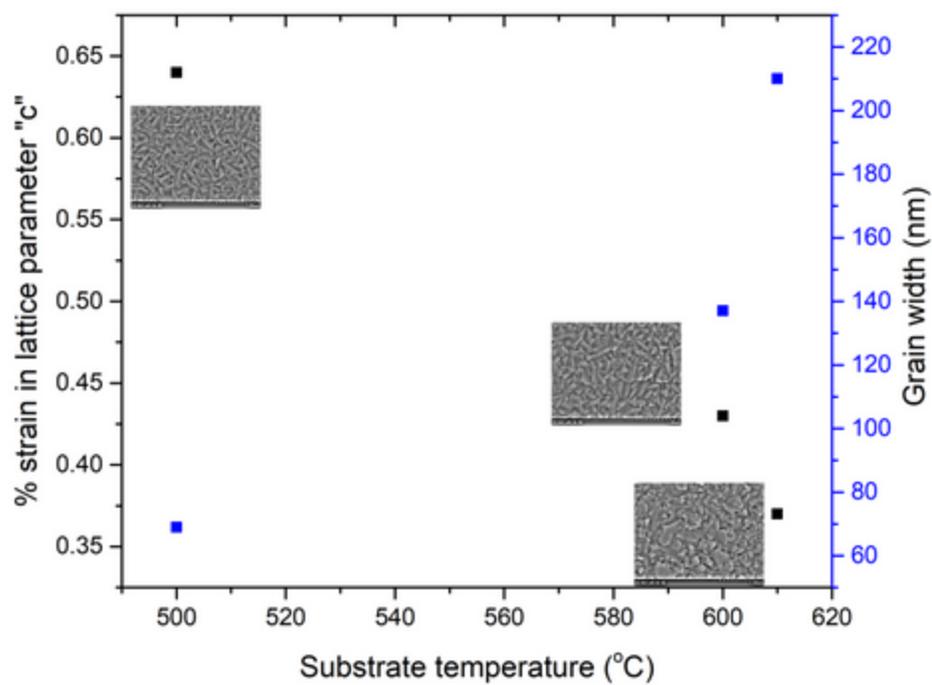
Abstract

Lattice strain in perovskites influences the proton conductivity by decreasing the trapping effect of protons with the oxygen. Strain in thin films is usually created by lattice mismatch, dopants, water absorption, or difference in thickness. Barium Cerate is studied due to its high proton conductivity at reduced temperature operation. New reproducible and simple processing routes for creating BaCeO₃ nanostructures at low temperatures will allow its structure control. BaCeO₃ orthorhombic phase (*Pnma*) is observed at room temperature. However, previous research shows the formation of a cubic phase of BaCeO₃ at 600°C when thin films were formed by e-beam vapor deposition.

In this research, BaCeO₃ thin films of high density were formed at 2 Å/s deposition rate by changing the temperature up to 610 °C. It was observed a pseudo cubic (*Pm3m*) structure when it was formed at 500 and 600 °C. After surpassing this temperature, the lattice parameter “c” changes due to the tensile stress originated from the grain growth. Then, diffusion of the atoms caused by tensile stress results in the formation of the orthorhombic structure with a dominant (002) orientation.

The degradation process of the films was also investigated. So far, the films are stable and not subjected to the formation of the BaCO₃ at room temperatures in atmospheric conditions.

The surface morphology and texture of the formed structures were observed by scanning electron microscopy. The crystallinity, phase transformation, and strain effect were investigated by X-ray diffraction peaks' displacements and peaks' presence. The dependence of the prevailing phases in the thin films, the crystal size, and texture coefficients on the technological formation parameters were also investigated.



Graph 1. % strain in lattice parameter "c" and grain width dependency with substrate temperature.

Keywords

proton conductor, texture, Orthorombic, lattice expansion

P1.43

Structure and properties of CrN/TiO₂ and CrN+Ox/TiO₂ coatings obtained in a hybrid technology combining PVD and ALD methods on substrates of austenitic 316L steel

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Abstract

Corrosion-resistant steels have an established and strong position in the market of structural and biomedical materials. Due to their properties, they enjoy unflagging interests. In particular, it is about strength and electrochemical properties and a relatively low price compared to other metal alloys with high corrosion resistance, such as titanium alloys. Therefore, scientific activities aimed at further improving their properties are justified. The study investigated hybrid coatings of CrN/TiO₂ and CrN+Ox/TiO₂ type obtained using the hybrid PVD/ALD technology on a substrate made of Cr-Ni-Mo (316L) steel. Coatings of CrN and CrN+Ox were obtained by the PVD method in the optimized technological conditions of the process. TiO₂ using *atomic layers deposition* was investigated. They were deposited at a variable number of cycles from 200 to 1000 cycles at a constant temperature of 200°C. Structural studies using scanning and transmission electron microscopy and atomic force microscopy were performed. The chemical composition analysis in the micro-regions was performed using EDS spectroscopy. The study of electrochemical properties was performed using potentiodynamic and electrochemical impedance spectroscopy (EIS) in a 3.5% NaCl solution. As a result of the study, it was found that the best anti-corrosion properties were shown by both hybrid coatings for which the TiO₂ layer was obtained in 500 ALD cycles. Based on microscopic studies with diffraction and spectroscopic analysis, the structure of the tested coatings was related to electrochemical properties, and the influence of deposition conditions on corrosion resistance was explained. In addition, the tests were supplemented with tests of tribological properties and adhesion of coatings to the substrate.

Keywords

PVD, ALD, hybrid coatings, corrosion resistance

P1.44

Exploring high-precision methods for the design of functional layers of aluminum doped zinc oxide: programmed co-precipitation and aerosol jet printing

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Abstract

High reproducibility of both microstructural and functional properties is often required when using materials doped at a level of few atomic percent, for example, as in the case of doped oxide materials. Moreover, the application of these materials calls for precise protocols of synthesis and deposition of the layers important in such applications as gas sensors to provide low device-to-device variation stemming usually from variation in composition and non-uniformity of the deposited layers.

Here we study the synthesis of x%Al:ZnO nanoscale oxides system (where x = 0.5, 1.0, 1.5, 2.5, and 5.0%) by programmed co-precipitation method optimizing the concentrations of aluminum and synthesis conditions to be further applied for sensing of volatile organic compounds. The obtained oxide powders are thoroughly characterized (XRD, STA, SEM, TEM, Raman spectroscopy) and utilized for the preparation of dispersions for aerosol jet printing of microstructures on multielectroded chips further employed for evaluation of their sensing performance.

The microstructure of the obtained oxide system appears to be significantly influenced by both the chemical composition of the product, i.e. the Al:Zn atomic ratio, and the conditions of synthesis yielding nanoparticles, and nanorods of various diameters and lengths. Using the obtained x%Al:ZnO powders, we have developed experimental protocols for the formulation of stable dispersions with rheological characteristics suitable for use as functional inks for aerosol jet printing and established optimal printing modes for achieving narrow (down to 50 μm) and homogeneous structures in the form of lines. The printed lines of 0.5%Al:ZnO demonstrated the best quality and fast sensing response to ethanol and acetone vapors mixed with air enabling detection of these compounds at the level of tens and hundreds of ppb and showing low sensor-to-sensor variations. This study is supported by grant of Russian Science Foundation № 21-73-10288, <https://rscf.ru/en/project/21-73-10288/>.

Keywords

aluminum doped zinc oxide, programmed co-precipitation, aerosol jet printing, gas sensor

P1.45

Effect of the palladium shell porosity in bimetallic Au-core Pd-shell nanoparticles on their radiosensitizing properties in anticancer proton radiotherapy

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Abstract

Metallic nanoparticles are increasingly used in biomedicine. A significant potential of such nanoparticles is the possibility of using them as compounds sensitizing cancer cells for radiation-based anticancer therapies. The radiosensitizing properties of nanoparticles are influenced not only by the size, shape and charge of nanoparticles, but also by their porosity.

For the purpose of our research, we obtained two types of bimetallic Au-gold Pd-shell nanoparticles. The so-called gold-palladium nanoraspberries (AuPd NR) had a porous structure of the palladium shell, while the gold-palladium core-shell (AuPd CS) had a continuous, non-porous palladium shell on the surface. For the physicochemical characterization of nanoparticles (morphology, chemical composition, nanostructure, concentration in solution, optical properties, charge) methods such as scanning transmission electron microscopy (STEM), energy-dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED), X-ray diffraction (XRD), nanoparticle tracking analysis (NTA), UV-vis spectra determination and zeta potential measurements were used.

Then, the effect of AuPd NR and AuPd CS as radiosensitizers in proton radiotherapy was investigated. In our study three colon cancer cell lines (SW480, SW620 and HCT116) with different malignancy potential were used. Normal colon epithelium cell line (CRL-1790) was applied as control. These cells were cultured with both types of NPs and then irradiated by a proton beam with a total dose of 15 Gy. The MTS and the annexin V binding test were used to evaluate the effectiveness of the combined proton irradiation. Thanks to the Nanolive 3D holotomographic microscope, the differences in the dynamics of penetration of nanoparticles into the cells were assessed.

The results of our research showed that AuPd-assisted proton radiotherapy is more effective than standard proton therapy, while the radiosensitizing properties of AuPd NR - due to the strongly developed surface of the palladium shell - were definitely better compared to AuPd CS.

Keywords

Nanoparticles porosity, Bimetallic nanoparticles, Proton therapy, Radiosensitizers

P1.46

WO_{3-x} thin films with Al, Pt Au and Mo doping: searching for piezoelectricity

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Abstract

The present research work focuses on the manufacture of WO₃ thin films doped with Al, Pt, Au and Mo with a thickness in a range of 150 nm – 250 nm. The films were deposited by radio-frequency sputtering at 225 W of RF power from commercial (99.9 %) WO₃ targets, and processed to post-deposition heat treatments ranging from 400 °C to 600 °C. In order to understand the influence of metal doping and heat treatments in the crystallographic structure and variation in the chemical composition that contribute to the induction of piezoelectric behavior in the films surface, an extensive characterization has been carried out using piezo force microscopy (PFM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy, X-ray emitted photoelectron spectroscopy (XPS) and atomic probe tomography (APT). APT revealed metal clustering in a distorted monoclinic (γ -WO_{3-x}) structure providing the ion-diffusion mechanism facilitated by oxygen vacancies contributing to the measured piezoresponses. These results will broaden the panorama of applications of the material in sensors, actuators and other energy storage and harvesting devices that involve the use of piezoelectric behavior, in addition to semiconductor and chromogenic behavior.

Keywords

WO₃, piezoresponse, APT, structure

P1.47

The effect of water on plasma functionalization with oxygen of graphitic carbons

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Abstract

Modification of carbon materials with plasma is used to create surface functionalities, in particular various oxygen groups. However, the most popular methods for oxidation of carbons are based on a wet chemical treatment with concentrated acids. Work function is a surface sensitive parameter which is used to evaluate electron donor properties of materials, and as a descriptor of modification degree for materials' optimization for many applications. Excessive oxidation of carbon material may not be required, or even may be undesired, in which case the work function changes may serve as an indicator of the optimum modification degree of the surface. Surface oxidized graphitic carbons studied as electrode materials, adsorbents, membranes, etc., require their application in an aqueous environment. This is not an issue for wet chemical oxidation, but plasma oxidized materials are often characterized in terms of their chemical and physical properties, most notably a degree of functionalization, after plasma treatment, but before immersion in water. Discrepancy arises, because plasma oxidized carbons show a time-dependent decrease of the degree of functionalization and related properties. We addressed the question of the degree of plasma-induced changes of powder graphitic carbon materials and their evolution after immersion in water. We used low temperature plasma oxidation with pure oxygen and carbon dioxide, and oxidation with concentrated nitric and sulphuric acids as reference treatments. To evaluate the electronic properties, the work function changes were measured for plasma treated samples, just after plasma modification and after immersion in water, and as references - acid oxidized. We show that immersion in water drastically decreases work function of plasma treated samples, which is accompanied by a decrease of the surface concentration of oxygen functional groups and radicals introduced by plasma. At the same time, the stability of acid treated samples drastically decreases, while for plasma modification it does not.

Keywords

oxygen functional groups, plasma, work function, stability

P1.48

Dual-curable crosslinking by isocyanate crosslinker with amine-based blocking agent for eco-friendly automotive clearcoats

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Abstract

The low-curing temperature to save energy and cost is the key issue in industrial curing processes for automotive clearcoats. Recently, simultaneous dual-curable crosslinking of clearcoats, which can be applied under low-temperature curing condition, has been extensively studied in academia and industrial fields. The thermally dual-curable crosslinking includes the urethane reaction between isocyanate (NCO) group in an isocyanate crosslinker and hydroxyl (OH) group in a dual-curable binder (here, hydroxyl-functionalized urethane methacrylate oligomer, HFUMO) and the free radical reaction of C=C bonds in the HFUMO by thermal radical initiator (TRI). Moreover, considering the environmental concerns, the emission of volatile organic compounds (VOCs) should be strictly tuned during the curing process of clearcoats. For eco-friendly clearcoat systems, in this study, the dual-curable isocyanate crosslinker blocked with amine-based blocking agent was newly synthesized by adding methacrylate functional group to the blocking agent. It is expected that the emission of VOCs could be significantly restricted during the thermal curing process through the direct participation of the methacrylate group in the blocking agent in the free radical polymerization. Real-time crosslinking behaviors of clearcoat coatings including the synthesized isocyanate crosslinker were monitored using rotational rheometer and rigid-body pendulum tester (RPT) under various thermal curing conditions (120 – 150 °C). Surface mechanical properties of cured thin clearcoat films produced at various temperatures were compared to check the low-temperature curing application, employing nano-indentation and nano-scratch testers. Especially, the emission of VOCs during the thermal curing was measured through a thermogravimetric analysis (TGA). Above properties exerted by newly-developed dual-curable clearcoat were compared to those by clearcoat with a commercial crosslinker (PL350), confirming that the new dual-curable isocyanate crosslinker could be beneficial to formulate eco-friendly automotive clearcoat systems.

Keywords

Automotive clearcoat, Thermal dual curing, Blocked isocyanate, Eco-friendly coating

P1.49

Characteristics of Photoinitiated Cationic Ring Opening Polymerization of Aliphatic Monomers with Induction Period during UV Curing

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Abstract

The ultraviolet (UV) photo-polymerization systems can provide many advantages over conventional thermal curing systems, considering the solvent-free reaction even at room temperature. Among the available photo polymerizations, the cationic ring opening polymerization (CROP) is well known to be insensitive to oxygen, preventing the undesirable side defect during the free radical polymerization. In this study, the reactivity of organic coatings containing four monomers (based on epoxy and oxetane) and two types of photo acid generators (PAGs) was investigated, focusing on rheological and mechanical properties. The real-time crosslinking behaviors of CROP monomers were monitored using a rotational rheometer. Furthermore, the ring opening reactivity of monomers protonated by PAGs was correlated with the induction period for initiating CROP reaction, employing the real-time Fourier transform infrared spectroscopy (RT-FTIR) with *in situ* UV irradiation and the differential scanning photo calorimetry (photo-DSC). Finally, the optimal content of monomer and PAG was determined from surface mechanical and adhesion properties of cured films measured via the nano indentation, nano scratch, and adhesion tests.

Keywords

Ultra-violet curing, Cationic ring opening polymerization, Crosslinking behavior, Induction period

P1.50

Temperature and thickness dependent dielectric functions of MoTe₂ thin films by spectroscopic ellipsometry

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Abstract

As a Mo-based transition metal dichalcogenides (TMDCs), the 2H phase MoTe₂ thin films with trigonal prismatic coordination is semiconducting, while the 1T' phase MoTe₂ monolayer is a 2D topological insulator and the bulk 1T' phase MoTe₂ is expected to be a Weyl semimetal. Here, we investigate the dielectric functions of 5–25 nm 2H phase MoTe₂ thin films over temperatures from 100 K to 450 K and energy range of 0.73–6.42 eV by spectroscopic ellipsometry. Results in Figure 1(a, b) show that, as for the center energies of excitonic peaks, when the thickness increases from 5 nm to 25 nm, A–C peaks gradually decrease, but the D–F peaks remain basically unchanged. As for the strengths of imaginary dielectric function, when the thickness increases, the strengths of A–C peaks gradually increase, but the strengths of D–F peaks show a complex evolution trend. Besides, as presented in Figure 1(d), the center energy of peak A in 10 nm MoTe₂ shows a Bose-Einstein attenuation trend when the temperature increases from 100 K to 450 K. With temperature increasing, Figure 1(c) shows that the strengths of A–D peaks in imaginary dielectric function gradually decrease, but the strengths of E, F peaks in imaginary dielectric function gradually increase. Understanding the temperature and thickness dependent dielectric functions of MoTe₂ thin films can enhance the physical understanding on the fundamental optical/electrical essential of 2D MoTe₂, and can also promote the design and performance of MoTe₂-based photoelectric devices.

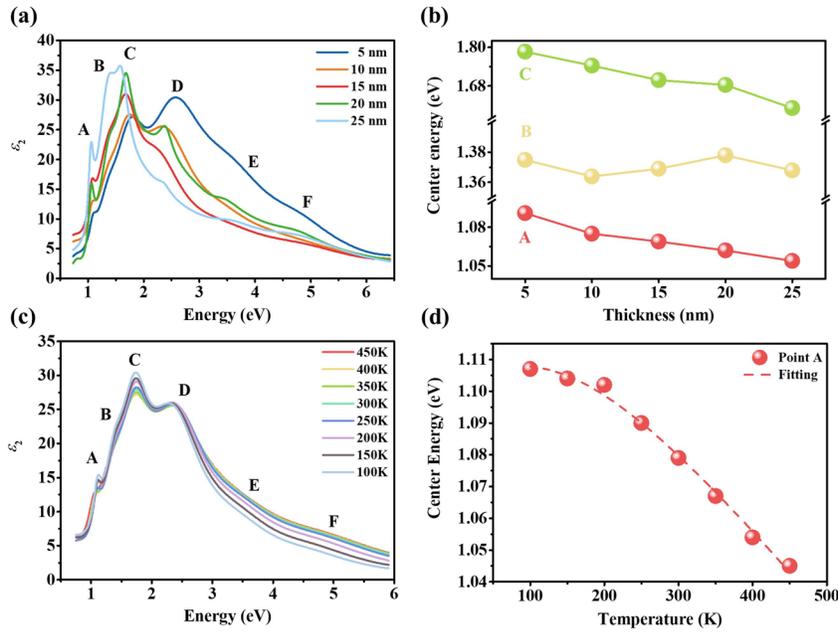


Figure 1. (a) Dielectric functions of 5–25 nm MoTe₂ thin films. (b) Evolution of center energies of feature peaks A–C with thickness increasing. (c) Dielectric function of 10 nm MoTe₂ thin film from 100 to 450 K. (d) Evolution of center energies of feature peak A with increasing temperature.

Keywords

MoTe₂, dielectric function, temperature effect, spectroscopic ellipsometry

P1.51

The effect of shot peening on the adhesion properties of Cr-N layer produced by double-glow plasma alloying

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Abstract

A method of using shot peening and double-glow plasma alloying was employed to produce conditions necessary for a sound bond between an Inconel 718 alloy and Cr-N coating. The interfacial roughness offers a means of producing additional contact areas between dissimilar materials. After double-glow plasma alloying and nitriding, a gradient Cr-Fe layer (around 20 μm) and a thin (1–2 μm) chromium nitride layer mainly composed of the Cr_2N phase was formed on the surface. The nitrogen adsorption energy on the Cr (200) surface was lower than that on the Cr (211) surface, which indicates that the nitrogen process can be divided into two independent steps. The hollow cathode discharges were evaluated under the different polar distances for deposition Cr layers. Three basic stages are required in the double-glow deposition processing: vaporation or destruction, atomization, and ionization. As regards the adhesion of the obtained Cr layers, decreasing the polar distance can improve the mechanical properties because of the ion reciprocating impact between the target and the sample surface. After the corrosion test, the interfacial contact resistance was measured to determine the effect of nitriding on the electrical conductivity of all samples. According to the corrosion results, the shot peening pretreatment Cr-N layer showed a low corrosive current density.

Keywords

Double-glow plasma alloying , Corrosion tests, Adhesion, Cr-N layer

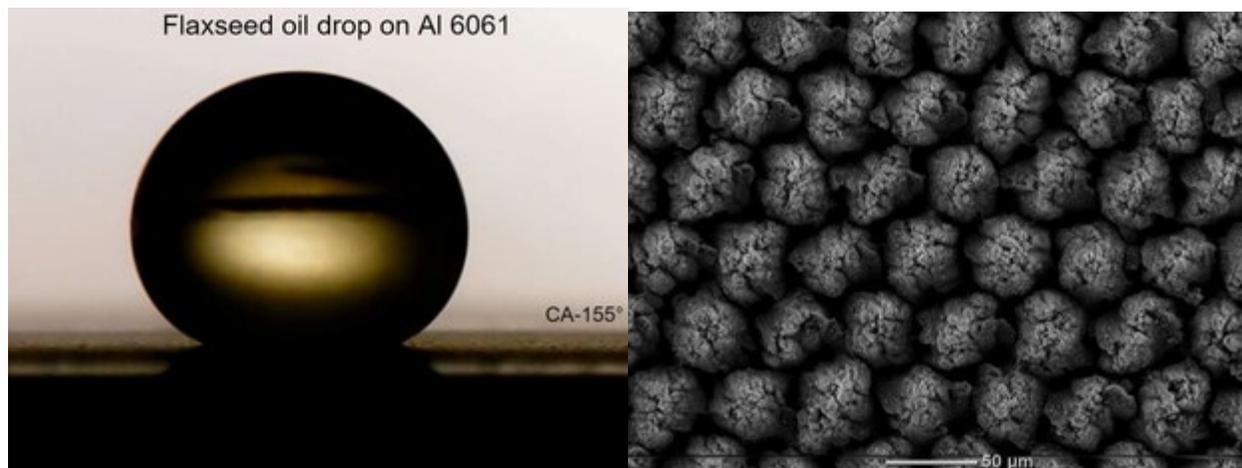
P1.52

Superamphiphobic aluminium surfaces obtained by nanosecond laser patterning: towards a scalable and cost-effective process

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Abstract



Laser modification on Aluminium

To obtain superhydrophobic surfaces, laser micromachining stands apart in comparison to competing surface modification techniques such as sol-gel, acid etching and micro/nano-lithography. Indeed, its features make it attractive for industrial viability: spatial selectivity, non-ultraclean fabrication conditions requirements, and its environmentally friendly approach. Ultrafast lasers are commonly used to generate specific micro-nano structures on metals due to lower Heat Affected Zone (HAZ) resulting in improved modification control. These specific surface features such as micro bumps and pillars support a stable Cassie state which enables fabricating oil-repellent surfaces. Ultrafast laser systems (pico and femtosecond) are costly, non-portable and with high maintenance costs, making it difficult to support large scale industrial production. This work, therefore, uses a readily available and cost-effective industrial nanosecond Infrared (Master Oscillator Power Amplifier) fiber laser to generate hierarchical micro/nano-textured surfaces on Aluminium alloy. Unlike conventional scans involving single or cross beam scan pattern, this work uses a triple scan approach resulting in the desired surface microstructure. Furthermore, two different methods were used to lower surface energy of laser textured surfaces: fluoroalkyl silane (FAS) treatment and a vegetable oil-based coating followed by thermal treatment for a more green-chemistry based approach. With both approaches, we obtained superhydrophobic surfaces

(contact angle (CA) >160 and CA >150 respectively). The generated superhydrophobic surfaces were compared and studied for their evaporation triggered wetting transition, plastron stability and corrosion resistance. By extensive exploration of the different parameters of the laser processing which includes laser repetition rate, scan line spacing, laser power and scan speed, we were able to obtain superhydrophobic and even superamphiphobic surfaces, repelling even low surface energy liquids such as vegetable oils. The results from this work can contribute to reduced production costs for fabricating highly performing superhydrophobic surfaces leading to a wider adoption at an industrial and commercial level.

Keywords

Superamphiphobic Aluminium, Nanosecond laser texturing, Plastron stability, Multi-scale surface

P1.53

Evaluation of the elimination of pharmaceutically active compounds by hyperbranched lignin polymers

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Abstract

The continuous release of pharmaceutical products to the environment has become a major concern as they are increasingly used in human and veterinary medicine. The presence of these pollutants in low concentrations in the water (between ng/L and µg/L), makes their detention and disposal very difficult, putting at risk the reuse of treated wastewater as well as the sustainability of the water cycle. The European Union reported the use of approximately 3,000 types of pharmaceutical products actives (PhACs).

The aim of this work was first to obtain hyperbranched polymers derived from a biodegradable residue such as Eucalyptus Kraft Lignin (KL), which has been used as raw material in the preparation of sorbents for the treatment of water contaminants. Lignin is an abundant raw material as it is a waste from the papermaking industry. In this research, the lignin structure was modified with the incorporation of nitrogen heteroatoms, changing its morphology and improving the selectivity towards contaminants such as pharmaceuticals, which are trapped inside internal cavities. The methodology applied to oxidize KL consisted of working under acidic conditions with H₂O₂, obtaining oxidized kraft lignin (OKL), to increase the active sites in KL, later, it was cross-linked with nitrogen heteroatoms, using urea-formaldehyde (OKLU).

To confirm the modification of the KL structure, different characterization techniques were used such as FTIR analysis, SEM, ³¹P NMR and N₂ (77 K). Finally, elimination of a series of different classes of pharmaceuticals (antibiotics, anti-inflammatories, psychiatric drugs and stimulants, lipid regulators, diuretics, and others) from the water was tested using KL and OKLU. The conditions used to perform sorption experiments were: concentration of pharmaceuticals = 100 ppb, temperature = 20 °C and amount of sorbent = 50 mg. quantification of the PhACs was performed by ultra-performance liquid chromatography coupled mass spectrometry (UPLC-MS/MS).

Keywords

Hyperbranched polymer, Kraft lignin, Pharmaceutically active compounds, Bioadsorbent

P1.54

Tuning the band gap and excitonic strength of monolayer SnSe₂ by substrate effect

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Abstract

Recently, monolayer metal dichalcogenides (MDCs) with low toxicity and cost have received much attentions due to their specific optical and electronic properties, e.g., high exciton binding energy, tunable band gap and high on/off ratio. As a typical MDC, SnSe₂ has been widely applied to the manufacture of optoelectronic devices owing to its high responsivity and external quantum efficiency in 2D structure. Due to reduced dimensionality and weak dielectric screening, Coulomb interactions of monolayer SnSe₂ are enhanced compared with bulk counterpart, which immensely increase the quasiparticle bandgap and the exciton effect. From previous report, the theoretical exciton binding energy of monolayer SnSe₂ is as high as 0.9 eV by the effective mass theory of 2D excitons, which indicates that it has enormous potential to tune the band gap and exciton effect of monolayer SnSe₂ through substrate effect.

In this work, the PBE, HSE06 and GW band structure of monolayer SnSe₂ whose indirect bandgaps are 0.79eV, 1.39eV and 1.69eV were calculated, as showed in Fig. 1(a), 1(b) and 1(c). Figure 1(d) is the imaginary dielectric function of freestanding monolayer SnSe₂.

We determined the quasi bandgaps and optical properties of monolayer SnSe₂ on Cu, sapphire and quartz substrates by scanning tunnelling spectroscopy and spectroscopic ellipsometer. From exciton peaks determined by critical point analysis of the dielectric function, the variation in exciton binding energy influenced by different substrates was confirmed. Theoretical results of quasi band structure and exciton binding energy on monolayer SnSe₂ with substrate effect correction were calculated by GW and GW-BSE methods. By combining experiment and theoretical results, the substrate effect on the optical transition of monolayer SnSe₂ was further clarified.

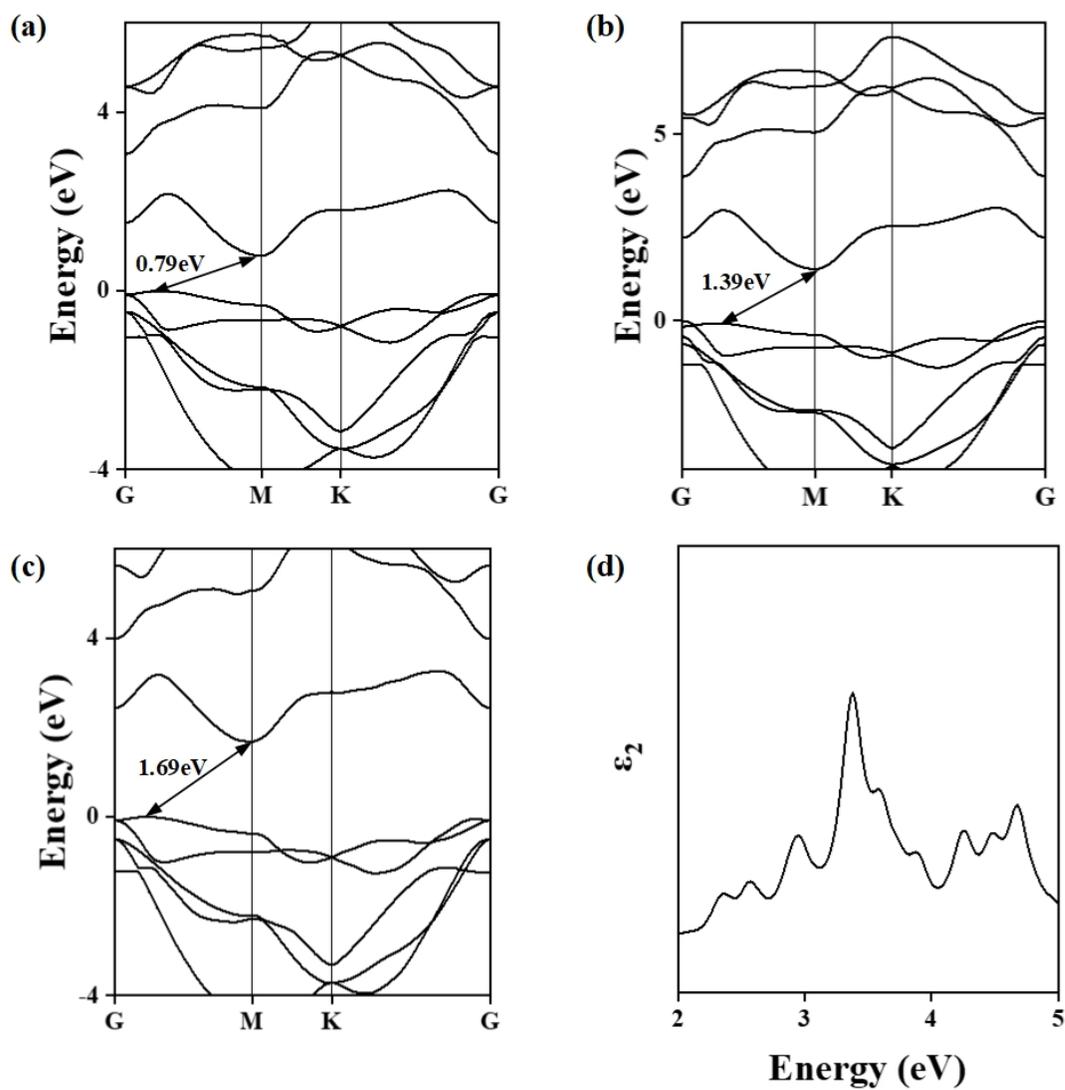


Fig.1 Band structures of the monolayer SnSe₂ calculated by PBE (a), HSE06 (b) and GW (c). (d) the imaginary dielectric function of monolayer SnSe₂ by GW-BSE.

P1.55

Surface contact charge formation mechanisms on polymers and triboelectric nanogenerators

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Abstract

Triboelectric nanogenerator (TENG) devices recently has gained a top importance for mechanical energy harvesting to power autonomous microdevices and portable electronics. TENG devices are consisting from oscillating electrodes covered with polymer film. When polymer is contacted-separated, the triboelectric charge is forming on surface. Charges on polymer in turn provide electrostatic induction in conductive electrodes. The potential difference between two connected electrodes with positive and negative charges drives current flow. The output from TENG is dependent from the magnitude of surface charge forming on polymer after contact-separation.

There has been a lot of discussions around the mechanisms of polymer triboelectrification. The three main mechanisms considered for polymer electrification are: (i) electron transfer, (ii) heterolytic covalent bond break and material transfer, and (iii) ion transfer between surface water adsorbate layers.

Recently we have executed a vast number of triboelectrification experiments, measuring charge density for more than 300 material combinations. We have studied various polymers with different structural state, surface adhesion and morphology, as well as nanoparticle additives. Through the investigation of these interfaces, clear evidence of material transfer via heterolytic covalent bond cleavage (heterolysis or heterolytic fission) is provided. Based on these results we have developed, a generalized model considering the mechanics of polymers as the critical parameter for triboelectrification, as well as have provided a correlated physical property to understand the triboelectric series. Material transfer must be accounted for when discussing the source of charge generated by polymers in TENG devices.

The established understanding of contact electrification provides a new paradigm for developing high performance materials for applications in triboelectric mechanical energy harvesting. As a such, we demonstrate several strategies (macromolecular structure design; selection of correct combination of mechanical properties and morphology between contacted polymer films; etc.) to strongly enhance the performance and efficiency of TENG device.

Keywords

Triboelectric nanogenerator, Contact electrification, Soft mechanical energy harvesters, Polymer

P1.56

OPTICAL STUDIES OF THIN FILMS OF CRYOCONDENSED MIXTURES OF WATER WITH CARBON DIOXIDE

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Abstract

Studies of thin-film structures of mixtures of water and carbon dioxide at various concentrations, condensing at low temperatures ($T = 11 - 80$ K) on the substrate. We can also spectroscopically identify carbon dioxide clathrate hydrate to see if clathrate formation is ubiquitous. Taking into account the widespread use of carbon dioxide and water ice in astrophysics. The specific configuration of the clathrate hydrate structure is identified through the ν_3 absorption band splitting which produces a band at $4.26 \mu\text{m}$ (2347 cm^{-1}) for molecules trapped in small cages and a band at $4.28 \mu\text{m}$ (2334 cm^{-1}) for molecules trapped in large cages. It appears that the aspect of the ν_3 absorption band is strongly influenced by physical (roughness, thickness, mixing properties) and optical (n and k) characteristics of the sample [1–3]. In this work, the refractive indices and FTIR-spectra of mixtures of water with carbon dioxide obtained by the PVD method were carried out. Deposition temperature $T_d = 11$ K. Pressure of the gas phase of the mixture during cryoprecipitation is $P = 10^{-4}$ Torr. The concentration of water in the mixture ranges from 5 to 95%. The IR spectral range of measurements was $370\text{--}7800 \text{ cm}^{-1}$.

Biography:

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Keywords

thin-film, cryocondensed, water, carbon dioxide

P1.58

Electrical properties, thermal stability and microstructure of metal-silicide/Cu Schottky contacts to AlGaIn/GaN-on-Si heterostructures

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Abstract

The outstanding material properties of GaN as well as the high mobility of carriers in the two-dimensional electron gas associated with AlGaIn/GaN heterojunction allows development of new efficient electronic devices operating at high-power and high-frequencies. AlGaIn/GaN-based high-electron-mobility transistors (HEMTs) are emerging as the next-generation of power devices. The recent progress in the quality of GaN-on-Si epitaxial layers offers a chance to reduce manufacturing costs by adapting fabrication process to the requirements of well-established Si foundries.

The reliability of AlGaIn/GaN HEMTs strongly depends on the performance of Schottky contact. Typically, the Ni/Au stack is used. However, in order to achieve better compatibility with Si technology, the presence of gold in fabrication processes should be avoided.

Copper, which has low resistivity and high thermal conductivity can be proposed as a substitute for gold in device interconnections, but due to high Cu diffusivity the Cu containing devices can be thermally unstable. Therefore, new solutions are required.

The silicide based Schottky contacts to AlGaIn/GaN heterostructures constitute a relatively unexplored field. Metal-silicides are thermally stable compounds with low resistivity and one can expect their reliable performance as well as their diffusion limiting capabilities.

In this work the properties of silicide/Cu contacts to AlGaIn/GaN heterostructures were studied in detail. Planar Schottky diodes utilizing various silicides (like Pd₂Si, Ni₂Si, CoSi₂, TiSi₂) with Cu as the top-level metal were fabricated on commercially available AlGaIn/GaN-on-Si heterostructure.

The properties of the fabricated layers and metal-semiconductor contacts were investigated by temperature dependent current-voltage and capacitance-voltage measurements, internal photoemission spectroscopy and transmission electron microscopy. The thermal stability of various silicide/Cu based contacts are studied and compared. The potential applicability in AlGaIn/GaN-on-Si HEMTs is discussed.

Keywords

Schottky contact, AlGaIn/GaN-on-Si, metal silicides, HEMT

P1.59

Characterization of WO₃ nanostructures in different synthesis conditions for hydrogen production

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Abstract

Tungsten oxide (WO₃) is a n-type semiconductor with numerous applications in photocatalysis due to its abundance, non-toxicity, versatility and photoelectrical properties. The objective of this work is to characterize nanostructures of WO₃ varying the synthesis conditions in order to use them as photoanodes for photoelectrochemical (PEC) applications.

WO₃ nanostructures were synthesized by electrochemical anodization in an acidic electrolyte (methanosulfonic acid) under hydrodynamic conditions (375 rpm). In order to improve the properties of WO₃ nanostructures, different complexing agents (0.05M H₂O₂ and 0.1M citric acid) were added to the anodization electrolyte. Furthermore, in order to obtain crystalline nanostructures, an annealing treatment was carried out after the anodization process, in which the heating temperature was also studied (400 °C, 500 °C and 600 °C).

With the aim of analyzing accurately and comparing the effect of both, the complexing agent and the annealing temperature, Field Emission Scanning Electron Microscopy (FE-SEM) and Confocal Laser-Raman Spectroscopy have been used to study the morphology and composition and crystallinity, respectively. Furthermore, in order to study the photoelectrochemical properties of the samples stability test were also performed.

Finally, once the optimal nanostructures were obtained, they were applied as a photoanode for energy production in photoelectrochemical water splitting tests, presenting a high photocurrent density response.

Acknowledgments

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Keywords

WO₃, nanostructures, anodization, photoelectrochemical

P1.60

Synthesis and analysis of drug-eluting hydrogel coating for urological guide wire

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Abstract

The urological guidewire is the most frequently used device during endourological procedures. It is the first tool introduced into the ureter during kidney surgery, where it is used to navigate other instruments (e.g., ureteroscope) through the ureter to the kidney. In many cases, the lumen of the ureter is too narrow for a ureteroscope to pass, leading to interruption of surgery, insertion of a ureteral stent, and repeat surgery after a short period of time. This complication is detrimental to the patient's health and unprofitable for the hospital. Therefore, we propose an isoprenaline eluting hydrogel coating, with an ultra-low friction interface, for PTFE urological guidewire surface modification characterized by the ability to remove ureter atresia for 5 minutes after insertion. The polyvinylpyrrolidone (PVP) hydrogel coating synthesis method is based on free-radical macromolecular grafting–crosslinking. The isoprenaline is loaded to the coating by immersing the product in a drug solution. We investigated the influence of the reagents concentration and process conditions on the properties of the obtained coating and the kinetics of drug release. Different variants of the isoprenaline release profile were obtained, depending on the structure of the coating. Moreover, coating additives were introduced and tested on artificial urine, giving the ability to control the eluting rate and amount of isoprenaline release over time. Thusly, the total amount of drug eluted over 10 minutes can be tailored from 0,7 up to 30 mg. The guidewires with different isoprenaline eluting profiles were fabricated and successfully tested in preclinical studies on the pig model.

Keywords

Urological guide wire, Local anaesthesia, Isoprenaline, Low-friction

P1.62

Influence of Temperature during the ZnO Electrodeposition on TiO₂ Nanosponges

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Abstract

Titanium dioxide (TiO₂) is one of the most widely used photocatalysts due to its good electronic and chemical properties. However, its high band gap (3.2 eV, $\lambda=390$ nm) limits its light absorption to ultraviolet range. In order to solve this problem, TiO₂ can be combined with other materials, such as zinc oxide (ZnO). When irradiating TiO₂/ZnO nanostructures with light, an exchange of electrons occurs between the conduction and valence bands of TiO₂ and ZnO, which reduces the recombination processes thus increasing the photoelectrochemical activity of the nanostructures.

In this work, the synthesis of TiO₂/ZnO hybrid nanosponges was carried out by electrochemical anodization of metallic titanium under hydrodynamic conditions (3000 rpm) in a glycerol/water (60/40 vol%) electrolyte with a concentration of 0.27 M NH₄F. Subsequently, ZnO was electrodeposited at -0.86 V_{Ag/AgCl} for 15 min using Zn(NO₃)₂ solutions of 1 and 10 mM at 25, 65 and 75 °C. The ZnO electrodeposition was performed after annealing the TiO₂ nanostructures (450 °C), that is, on crystalline TiO₂. The samples were characterized by [Field-Emission Scanning Electron Microscopy \(FESEM\) with Energy-Dispersive X-Ray spectroscopy \(EDX\)](#), [X-Ray Diffraction \(XRD\)](#) and [X-Ray Photoelectron Spectroscopy \(XPS\)](#). In addition, photoelectrochemical water splitting tests were performed under dark and illuminated (AM 1.5) conditions to evaluate the photoelectrochemical activity of nanostructures.

The photoelectrochemical response of the TiO₂/ZnO hybrid nanosponges improved as the electrodeposition temperature increased in the range of 25-75 °C, both for a concentration of 1 and 10 mM. The best results were obtained when performing the ZnO electrodeposition at 75 °C with a concentration of 10 mM. Under these conditions, an increase in photoelectrochemical activity of 275% was obtained.

Acknowledgments

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Keywords

TiO₂/ZnO hybrid nanosponges , ZnO electrodeposition , Temperature influence, Photoelectrochemical activity

P1.63

Investigations of wear and cavitation resistance of the cermet coatings manufactured by HVOF spraying

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Abstract

In this work, the comparison of tribological properties such as wear-resistance and cavitation erosion resistance of High Velocity Oxy Fuel (HVOF) sprayed coatings onto AZ31 magnesium alloy were examined. As a coating material, three commercially available powders: WC-Co-Cr (i), WC-Co (ii) and WC-Cr₃C₂-Ni (iii) were used. The results were compared with the AZ31 magnesium references sample in both tests. Cavitation tests indicate that in the initial stages of erosion, the WC-Co-Cr sample has slightly higher resistance than WC-Cr₃C₂-Ni and far better cavitation resistance than WC-Co coatings. In further stages of erosion, the Ni-containing coating delaminates due to its lower fracture resistance surface nonuniformities such as pores and ceramic-metallic phase interfaces. In the case of sliding wear, the results are strongly related to the mechanical properties. The (i) and (ii) samples exhibit higher hardness and higher values of Young modulus than (iii) one. These properties are crucial from resistance against wear point of view. Moreover, cobalt matrix exhibit better work conditions with counter-body, which could be seen in the COF values, approx. 0.3, whereas for nickel matrix one, it is about 0.4. The main wear mechanism relies on the detachment of cermet material, starting at microstructural cracks and discontinuities. Generated stresses with lower hardness values and Young modulus for (iii) sample results in lower value of wear factor, approx. $10 \cdot 10^{-8} \text{ mm}^3/\text{N}\cdot\text{m}$. For harder samples, which exhibit higher stiffness (i) and (ii), this type of wear results in lower values of wear factor: $6 \cdot 10^{-8} \text{ mm}^3/\text{N}\cdot\text{m}$ and $9 \cdot 10^{-8} \text{ mm}^3/\text{N}\cdot\text{m}$, respectively. The wear mechanism is affected by abrasion, growing and transfer of the material between counterball and coatings. Deposition of the cermet coatings effectively prevents the magnesium substrate, presenting very poor resistance to cavitation and sliding wear.

Keywords

wear resistance, cavitation erosion resistance, cermet coatings, High Velocity Oxy Fuel (HVOF)

P1.64

Bio-inspired H-bond cross-linking of nanostructured gelatine by inorganic goethite α -FeOOH nanowires

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Abstract

Gelatine material is suitable for tissue scaffolds because exhibits appropriate surface chemistry and mechanical properties, as well as porous and nanostructured microstructures can be easily obtained. Gelatine implies advantages such as high “activity”, biocompatibility and non-toxicity that are suitable for fibroblast culture to provide skin wound healing and dermal reconstruction. However, nanostructured gelatine is water-soluble. At the same time, cells are seeded on the scaffolds in the aqueous environment and thus the scaffolds must be insoluble in water to maintain structure and provide mechanical support to cells during tissue growth. To make gelatine insoluble, cross-linking can be carried out by various chemical, enzymatic, and physical methods. However, the covalent bonds in gelatine are created using the same groups that are biologically “active”. In nature, when there is tissue damage, the first cells that arrive at the site start hydrolysing collagen into gelatine because it presents more sites for attaching the next waves of cells that come to tissue regeneration. This means that gelatine that is not chemically crosslinked could be excellent in tissue engineering and wound healing because the excellent bioactivity of the surface of gelatine is not altered. In the present work, we are demonstrating an approach to deliver water-insoluble gelatine via hydrogen bonding by using goethite α -FeOOH nanowire additives. The crystal surface of goethite is densely covered with -OH groups, thus ensuring sites for hydrogen bonding with gelatine. Inorganic goethite nanowires provide nanostructured hydrogen-bond cross-linked gelatine that does not dissolve in water. Moreover, goethite has shown visible light-controlled desorption behavior, which potentially could allow disintegrating the gelatine by visible light once the cells have grown onto it, thus providing all different kinds of possibilities for manipulating the system for tissue engineering purposes.

Keywords

gelatine, scaffold, goethite FeOOH, bio-inspired

P1.65

The development of a novel universal coating for urological implants

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Abstract

Urological implants are widely used to treat diseases associated with the urinary tract system(UTS). However, their invasive nature is associated with challenges that include side effects such as uroepithelial tissue damage and increased frequency to urinate. In addition, their effectiveness is limited by infections. Most strategies employed to solve these challenges are designed for specific materials which inherently reduces their scope. Thus, this research was aimed at developing a coating for urological implants, which is characterized by a low friction coefficient with urinary tract tissues, possesses antimicrobial properties, and is adaptable to different materials used to fabricate urological implants.

The coating was developed on two different urological implant plastic polymers, polydimethylsiloxane (PDMS) and polyurethane (PUR) using polydopamine (PDA) as a versatile primer. Subsequently, the materials were coated with the hydrophilic polymeric material, polyvinyl pyrrolidone (PVP). This was followed by an assessment of stability, cytotoxicity, mutagenicity and antimicrobial properties. The developed coating was found to be none toxic via brine shrimp assay, not mutagenic according to the Ames test using T100 strains and possibly inhibited microbial growth (*Escherichia coli*) but was not bactericidal. Overall, the coating is a promising strategy to solve uroepithelial tissue damage caused by urological implants and may reduce infections. However, it should be coupled with an antimicrobial agent to improve its antimicrobial properties.

Keywords

Urological implants, Universal coating, Low friction co-efficient, Antimicrobial properties

P1.66

Structure and tribological properties of sputtered Cu-modified MoS_x:Cu films

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Abstract

Combining materials with a self-lubricating character is a promising approach for an environmentally friendly lubrication. Therefore, Cu was incorporated in HiPIMS synthesized non-stoichiometric MoS_x films. By increasing the Cu concentration from 3.09 ± 0.09 at.-% up to 31.93 ± 0.12 at.-% by an increased target power, the structure and the tribological properties were evaluated depending on the chemical composition. The results show, that an increased Cu content in the films in combination with the target setup during the deposition process leads to a preferred (002) basal-plane crystallite orientation and a densification of the microstructure in comparison to MoS_x. Due to these structural properties, the dry friction behavior is improved under humid conditions. In combination with the transferfilm formed on the surface of the 100Cr6 counterpart, the lowest coefficient of friction of $\mu = 0.092 \pm 0.003$ is seen at a target power of 1.5 kW. Additionally, Cu tends to agglomerate the generated wear particles, which contributes to a high amount of tribomaterial with a MoS_x character in the tribo track and thus a low wear. At a target power of 2.5 kW the lowest wear coefficients with $k = 0.64 \pm 0.22 \times 10^{-5}$ mm³/Nm for the coated sample and $k = 0.07 \pm 0.07 \times 10^{-5}$ mm³/Nm for the 100Cr6 counterpart were achieved. Therefore, the modification of MoS_x films with Cu is promising to reduce the sensitivity of the friction on the environment and improve the tribological properties.

Keywords

MoS_x:Cu, Basal-orientation, Friction, Transferfilm

P1.67

Towards plasmon mapping of SERS-active dewetted Ag nanoparticles using scanning probe energy loss spectroscopy

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Abstract

Surface-enhanced Raman spectroscopy (SERS) increases the sensitivity of conventional Raman by adsorbing target analyte molecules onto metal nanoparticles where optical fields can resonantly couple with localised surface plasmon resonances (LSPR). LSPR may be tuned, to optimise for analyte and probe wavelength, by changing the particle size, shape, spacing and composition. As this behaviour can be complex, having an experimental technique capable of directly imaging LSPR is extremely useful for developing SERS-active substrates. This project investigates the potential application of a scanning tunnelling microscope (STM)-based technique, scanning probe energy loss spectroscopy (SPELS), to map the plasmonic behaviour of SERS-active substrates. In SPELS, the STM tip is used to field-emit electrons that are backscattered from the sample surface and collected by an electron energy analyser to produce a spectroscopic map of energy loss features due to inelastic scattering events such as plasmon excitations. We report on our progress using Ag nanoparticles (NP) produced by thermal dewetting of silver thin films on SiO₂/Si and Ti/SiO₂/Si. The particle size distribution and interparticle spacing have been investigated as a function of deposition and thermal annealing parameters using atomic force microscopy. Addition of an adhesion layer resulted in a smaller mean particle size and interparticle gap under the same anneal conditions. SERS data of Rhodamine 6G dye show a correlation between SERS enhancement and the nanoparticle size and interparticle spacing, which is explored using finite-difference time domain (FDTD) simulations. SPELS measurements of these structures show wide variability in backscattered electron (BSE) yield during single image scans and energy-dependent contrast changes between the Ag and SiO₂ in BSE images that are attributed to the different electron emission angular distributions of the two materials at low primary electron energies. The impact of this contrast on the acquisition of spectroscopic plasmon mapping data will be discussed.

Keywords

Scanning Probe Energy Loss Spectroscopy, SERS, Dewetting, Plasmonics

P1.68

Covalent grafting of alkyl chains on nanosecond laser oxidized titanium surfaces through silanization and phosphonation methods

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Abstract

The grafting of organic molecules on the surface of titanium oxide films opens interesting possibilities to control the hydrophobicity and biocompatibility of titanium surfaces, and to develop self-cleaning surfaces, sensors, etc. Processing titanium surfaces by nanosecond lasers allows obtaining oxidation and complex micrometric surface patterning. This can improve the tribological properties and the adherence of polymer coatings densified through remelting. For high laser fluence, the oxidized surface layers have a stratified structure composed by titanium oxide nanoparticles deposited on top of compact oxide layers, where stoichiometric titanium oxides are progressively replaced in depth by sub-stoichiometric oxides and oxynitrides. Such layers bring to the surface Ti-OH groups which can be grafting sites for organic molecules.

This work evaluates the feasibility of silanization and phosphonation procedures for the grafting of organic molecules on the surface of nanosecond laser treated titanium. The silanization using alkoxysilanes with C12 and C18 alkyl chains was attempted in boiling THF solution, in pure liquid phase and in vapor phase. The phosphonation with octylphosphonic acid was performed in boiling water solutions. The treated surfaces were analyzed by Raman spectroscopy, EDS and XPS. Their hydrophobicity was evaluated using static contact angle measurements.

The silanization in THF resulted in only a partial monolayer coverage. The modification in pure liquid silane and in vapor phase allowed attaining higher load of grafted groups and the formation of polycondensed silane layers. The phosphonation in boiling water solutions allowed easily to obtain a significant P load. Both silanization and phosphonation increased the hydrophobicity of laser treated titanium surfaces. However, the treatment with octylphosphonic acid in water solutions is more suitable for grafting organic groups on the surface of laser functionalized titanium substrate since milder synthesis conditions and lower concentrations of the modifier are necessary to obtain similar organic load and hydrophobicity.

Keywords

laser surface treatments, titanium oxides, silanization, phosphonation

P1.69

Novel green deep eutectic solvents as efficiency absorbents for monoaromatic hydrocarbons capture from gaseous fuel streams

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Abstract

Monoaromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX) occur in various concentrations in gaseous fuel streams i.e. natural gas and biogas. Due to their toxic properties, carcinogenic character, shortening the lifetime of the catalysts, and potential emission to the atmosphere during combustion processes, BTEX has to be removed before further processing of fuel streams. One of the most popular methods of purifying fuel streams is physical absorption. However, the choice of a suitable absorbent is the key to the successful process application. Therefore, in this study, a new gaseous fuel treatment procedure based on physical absorption was developed. In order to meet all the requirements of green engineering, a new generation of deep eutectic solvents (DES) was tested. The studied DESs were composed of substances that can be easily extracted from natural sources, such as plants or biomass (including monoterpenes, carboxylic acids, furans). The main important physicochemical properties (i.e. viscosity, density, melting point) that affected the absorption process, were studied. The mechanism of DES formation and interaction between BTEX and DES were explained by means of theoretical and experimental study. The kinetics of the absorption process has been studied in detail. The most significant absorption parameters i.e. type of DES, gas flow rate, kind of matrix gas, temperature, and initial concentrations of BTEX were optimized. The obtained results indicate that DES composed of Eucalyptol, Carvone, and camphor as HBA and octanoic acid, as HBD in 1:1 molar ratio could absorb BTEX efficiently. The van der Waals interactions is the main driving force for the BTEX removal from gaseous fuel streams.

Acknowledgements

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Keywords

deep eutectic solvents, monoaromatic hydrocarbons, gaseous fuels, absorption

P1.70

Deep eutectic solvents based on symmetric quaternary ammonium salts for volatile organosulfur compounds removal from biogas

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Abstract

Currently, the bioenergy of biogas form is stating an alternative to sources conventional. Both agri-food and animal waste are used for the production of biogas, but also waste from landfills and sewage treatment plants. The obtained biogas, apart from the main component - methane, contains many other problematic pollutants. Volatile organosulfur compounds (VSCs) are particularly troublesome trace compounds, which are characterized by high toxicity, reactivity, and corrosive. In order to convert the biogas into high-quality biomethane, the removal of VSCs is necessary. At the present time, there are many conventional technologies to remove impurity from biogas. In physical absorption processes, VSCs can be selectively removed from a biogas stream by using appropriate solvents. However, solvents should be characterized by high absorption capacity, non-toxicity character, and easily regenerated. All these requirements are met by deep eutectic solvents (DESs). DES are compounds that consist of a Hydrogen Bond Acceptor (HBA) and Donor (HBD). During DES synthesis, specific interactions between HBA and HBD are formed, which affect to lower the melting point of the complex compared to pure substances. In addition, by mixing different HBA and HBD, it is possible to fine-tune the physicochemical properties of DES.

The paper presents the use of DES for removing VCSs from the biogas stream. In order to select the most effective absorbents, the theoretical model COSMO-RS was used. DESs characterized by the highest solubility of VCSs were synthesized, and their physicochemical properties were studied. In the further part of the studies, the experimental tests of absorption in a dynamic system were performed. The influence of several process parameters, i.e. temperature, biogas flow, initial VSCs concentration, and regeneration was investigated. The obtained results were compared with commercially available absorbents.

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Keywords

green solvents, deep eutectic solvents, biogas, volatile organosulfur compounds

P1.71

Mechanical properties of cavitation generators with CrN + WC/C and WC/C coatings intended for use in the cavitation environment

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Abstract

The main purpose of this publication was to describe in details the correlation between microhardness and scratch test results of the tested coatings deposited by PVD (Physical Vapour Deposition) method on the cavitation generators working in cavitation environment. First coating in the form of composite layer CrN+WC/C and second WC/C plate coating were deposited on two selected steels which already are used or can be use on constructional elements working in a cavitation wear environment. Steel P265GH is commonly used for pressure devices working at elevated temperatures, with a ferritic – pearlitic structure, and the other tested steel from a group of stainless steels, i.e. chromium – nickel X2CrNi18-9 (304L) steel with an austenitic structure due to its corrosion resistance, it can also be used in these conditions. The tests results obtained allow to conclude composite CrN+WC/C coating exhibit better adhesion than WC/C plate coatings deposited on the both tested constructional steels. A critical load value for the CrN+WC/C coating spans between 29 and 34N and is 35-40% higher than for the plate WC/C coating.

Keywords

coating CrN+WC/C, coating WC/C, cavitation, adhesion

P1.72

New polycatecholamine coatings and nanoparticles for various biomedical applications

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Abstract

Since its first report in 2007, polydopamine (PDA) has been widely investigated as a coating for many biomedical applications. PDA is a biocompatible, biomimetic polymer that can create a stable coating on virtually any material, hydrophilize its surface and be a base for the covalent bonding of many chemical compounds. It has been proven that PDA coating promotes the adhesion and proliferation of many types of mammalian cells, e.g., myoblasts, hMSCs, HUVECs, chondrocytes, HT1080 cells, on different materials, e.g., polyurethane, polydimethylsiloxane, polycaprolactone, poly(lactic-co-glycolic acid), poly(L-lactic acid), glass, stainless steel, and titanium. PDA is synthesized by oxidative polymerization of dopamine. We developed a new method of producing PDA analogues from other catecholamines: tyrosine, phenylalanine, and 2-phenylethylamine. Due to the much lower activity of dopamine analogues, additional oxygen sources were employed. We optimized the synthesis method and characterized our coatings using atomic force microscopy (AFM), scanning electron microscopy (SEM), UV-VIS and FTIR-ATR spectroscopy. We also studied the surface hydrophilization and measured coatings zeta potential. Our coatings showed similar properties to PDA, which allowed us to propose a synthesis mechanism for polycatecholamine coatings. We studied the adhesion and activation of platelets on new polycatecholamine coatings and demonstrated that they are hemocompatible. Cell cultures revealed that materials with polycatecholamine coatings showed much faster adhesion and proliferation of HMEC and HUVEC. As shown in Fig. 1, PTFE coated with polydopamine (PDA), polytyrosine (PTYR), polyphenylalanine (PFA), and polyphenylethylamine (PEA) is almost completely covered with HUVEC after five days of cell culture, contrary to the pristine PTFE, where only single cells can be spotted on the polymer surface. We also synthesized nanoparticles from polycatecholamines and studied their size and properties.

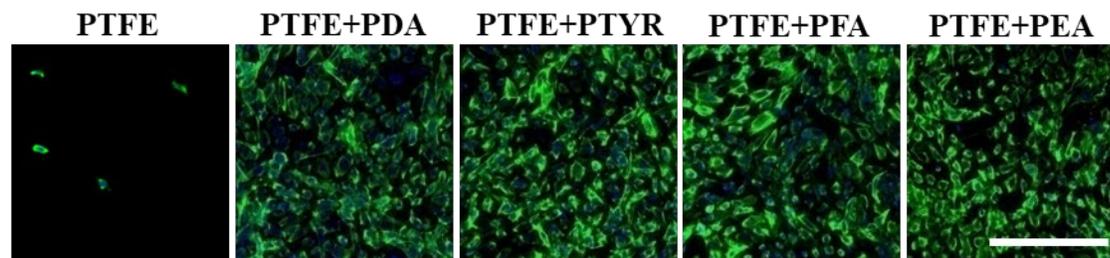


Fig.1. Confocal laser scanning microscopy images of 5-day HUVEC culture on PTFE coated with polycatecholamines. The scale bar represents 100 μm.

Keywords

coatings, polycatecholamines, polydopamine, tissue engineering

P1.73

Excited electron dynamics in thiophene-based polymers

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Abstract

Optically active thiophene-based polymers are promising candidates for solar cell, OLED or transistor (OFET) applications. An internal donor (D) – acceptor (A) system is formed by coupling thiophene polymers with pyrrole chains. The charge transport behavior can be tuned by different alkyl side chains since they influence the electronic structure, HOMO and LUMO level positions, and interchain interactions. A direct assessment of the intramolecular and intermolecular dynamics may guide synthesis routes. With diketopyrrolopyrrole – quaterthiophene (PDPP4T) and thienyl-diketopyrrolopyrrole-thieno-thiophene (PDPPTT) we investigated the electronic dynamics of verified high hole-mobility organic semiconductors. For the second polymer, the two thiophene rings were exchanged for thieno-thiophene in the backbone. In contrast, another polymer pF8T2 with bi-thiophene in the backbone was used, but with fluorene instead of pyrrole as acceptor. These different molecular configurations are intended to provide insights into the change in electron configuration due to both backbone modification and intermolecular packing.

We report results of temporally resolved photoemission studies on thiophene polymers on Si(100) substrates. Occupied electronic levels were analysed via static UPS. Dynamic 2PPE experiments were performed for the energetic position and dynamics of the unoccupied states. Details in the electron dynamics were resolved with the fourth harmonic of a 500 kHz fiber laser as probe pulse and IR and UV radiation from a NOPA as pump pulse.

The systems were studied as deposited by spin coating as well as after annealing to 180 °C. Before annealing, the electron kinetic energy resolved lifetimes range from a few 100 fs up to 3 ps, and show also a slow component around 15 ps. After annealing, the lifetimes shorten, thus witness an improved electron transport in the film.

Keywords

Pi conjugated donor – acceptor system , diketopyrrolopyrrole – quaterthiophene (PDPP4T) , thienyl-diketopyrrolopyrrole-thieno-thiophene (PDPPTT) , time resolved photoelectron spectroscopy

P1.74

Oxygen plasma surface functionalization of polyurethane towards improved biocompatibility

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Abstract

Polyurethanes are a large family of polymers widely used in medical devices with one common characteristic: urethane linkages along the molecular chains. They are among the best choices for biomedical applications due to their tunable properties. Polyurethane surfaces can be functionalized to meet the desired properties for specific applications. It can be achieved by applying plasma modification introducing surface functional groups with simultaneous control of their bulk properties.

Commercially available polyether-based polyurethane for medical applications was used in this study. The oxygen groups were introduced using a plasma generator, various modification parameters were tested (oxygen pressure in the chamber, generator power, modification time). No structural changes were found under the influence of plasma, but a strong change in surface properties influencing the biocompatibility of the tested polymer was observed (e.g. wettability). The unmodified material is hydrophobic ($\Theta_{H_2O} = 105^\circ$), and the completely hydrophilic surface is obtained at $p_{O_2} = 0.14$ mbar and $t = 4$ min. It was found that the most important parameter controlling the degree of modification of the polyurethane surface is the oxygen pressure in the generator chamber. The most important changes in functionalization stability were observed during the first day after modification (from totally hydrophilic surface to 30°). It is worth underlining that the initial value of the contact angle is not recovered, even after 28 days. To evaluate the biological response of the obtained surfaces, A549 cells and microbiological tests were carried out. The oxygen plasma-modified polyurethane improves the adherence of cells, whereas no significant changes in the number of adherent bacteria were observed. Additionally, bacteria exhibited a lower ability to produce biofilm on the plasma-modified surfaces. The results provide the background for the development of polymeric biomaterials with improved surface biocompatibility.

Acknowledgment: This study was financed by the Polish National Science Centre project DEC-2019/35/D/ST5/03107.

Keywords

polyurethane, plasma treatment , biocompatibility, surface functional groups

P1.75

On the friction coefficient on different kinds of snow of steel surfaces irradiated with ultra-short laser pulses

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Abstract

Ski bases for alpine skis are manufactured in ultra-high molecular weight Polyethylene (UHMWPE). While showing excellent sliding behavior on natural snow, these suffer severe abrasion and wear on artificial, highly compacted, up to icy, aggressive snows. Ski edges, that are made in a low carbon steel (C60), when sliding on slopes prepared with artificial, up to barred snow rapidly deteriorate. At high speed, edges warm up, thus inducing a localized temperature increase of the surrounding UHMWPE regions, causing permanent, irreparable damage of the base. This mechanism is particularly severe in competition skis.

A solution to the problem is to introduce hard, wear and oxidation resistant metallic materials, notably the stainless steel AISI 301.

We performed different surface treatments obtaining Laser Induced Periodic Surface Structures (LIPSS) on cold rolled, degreased AISI 301, with ultrashort laser pulses (wavelength 1030 nm, fluence 0.532 J cm^{-2} , 75% overlap of spot diameter both along X and Y) of duration between 247 fs and 7 ps, respectively. We characterized the morphology of the LIPSS with SEM. Contact angles, measured with water droplets, of the laser-treated surfaces indicate hydrophobic behavior, and are larger than that of the untreated AISI 301 surface.

We performed sliding tests on laboratory samples ($5 \times 5 \text{ cm}^2$, thickness 0.5 mm), using a custom-built snow tribometer, with different kinds of snow representative of realistic environment conditions, using a normal load that reproduces the pressure exerted by a skier of average weight. The trend of the measured friction coefficients for different ranges of ski speed are discussed and compared with those of UHMWPE bases prepared state of the art.

Keywords

Snow, Stainless Steel, LIPSS, Friction

P1.76

Mechanical behavior of ion-irradiated ODS RAF steels strengthened with different types of refractory oxides

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Abstract

Materials dedicated for IV. Gen of nuclear reactors must meet several rigorous requirements, i.e. improved mechanical properties at high temperature, high corrosion resistance, and outstanding stability under heavy radiation. One of the most promising candidates that may withstand exploitation in such an extreme environment is Oxide Dispersed Strengthening (ODS) Reduced Activation Ferritic (RAF) steel. It is known that by introducing refractory oxides to the ferritic matrix it is possible to obtain a brand new kind of materials with an excellent set of properties. In our work, we focused on verifying of structural and mechanical properties of materials strengthening by three different types of refractory oxides (yttria, alumina and zirconia) submitted to ion-irradiation. Ion irradiation is a common methodology that allows for introducing radiation defects into microstructure without activation of research materials. Thanks to this procedure it is possible to evaluate materials behavior in the simulated nuclear environment in a very safe and quick manner.

In this work, three types of materials with a basic chemical composition of 12%Cr, 2%W, 0.3%Ti, and strengthened with 0.3% Y₂O₃ or Al₂O₃ or ZrO₂ were produced by mechanical alloying and subsequently consolidated by Spark Plasma Sintering technique. Structural and mechanical properties were evaluated by implementing SEM/EBSD methodology, X-ray diffraction analysis, nanoindentation, micro-tensile tests and micro-hardness tests. Radiation damage effects were introduced to the microstructure of materials by ion irradiation using Fe⁺ ions with energy 250keV with three different fluences (up to 3x10¹⁶ ions/cm²). Mechanical and structural response of research materials was evaluated by TEM, Grazing Incident X-ray Diffraction, and nanoindentation tests. Obtained results have revealed a strong correlation between the type of strengthening oxide and materials' microstructural and mechanical behavior after radiation damage.

Keywords

ODS steels, ion irradiation, refractory oxides, mechanical properties

P1.77

W-doped VO₂ thin films prepared via sol-gel for application in energy-efficient smart windows

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Abstract

Thermochromic smart windows are based on the use of functional coatings that allow them to regulate the solar energy that passes through them in response to the external temperature. Among the thermochromic materials, monoclinic VO₂ is one of the most important. This dielectric phase of VO₂ is transparent to infrared radiation at room temperature and, at around 68°C, undergoes reversible structural changes leading to a tetragonal conductive metallic phase, rutile type VO₂. Under these conditions, it partially blocks NIR radiation, which causes temperature increase indoors, but retains its transparency in the visible range. The performance of a coating for this application is determined by three thermochromic parameters: 1) the phase transition temperature, T_c, which should be close to a comfort temperature, 2) the photometric light transmittance, T_{lum}, which should be constant and remain at a minimum of 60%, and 3) the solar modulation capacity, ΔT_{sol}, which should be at least 20%.

VO₂(M) thin films have been prepared via polymer assisted sol-gel route deposited by dip-coating onto transparent silica glass substrates. Subsequently coated glasses were heat treated in a controlled reducing atmosphere. The resulting samples have shown remarkable thermochromic behaviour. In order to solve the problem of the high transition temperature and to bring it closer to applicability, samples have been doped by adding controlled amounts of tungsten to the sols. The presence of tungsten in the initial sol modifies the crystal lattice of the monoclinic VO₂ giving rise to a decrease of T_c of around 20°C.

The samples have been characterised by UV-Vis-NIR, spectroscopic ellipsometry and AFM, SEM and TEM microscopies. In this way, the different thermochromic parameters have been related to the characteristics of the different samples.

Keywords

Vanadium dioxide, Thermochromism, Smart Window, Metal-insulator transition

P1.78

Linking macroscopic surface morphology of activated carbon fibers to their electrosorption capacity by electrochemical impedance spectroscopy

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Abstract

Activated carbon fibers (ACFs) are popular electrode materials for capacitive deionization (CDI) because of their ease of use and good adsorption capacity. It is well accepted that the surface morphologies have an enormous effect on contact interfaces of electrodes and current collectors, which affect the overall CDI performance. But it remains unclear how exactly the macroscopic surface morphology affects charge and mass transfer at the electrode/electrolyte interface of the CDI system. This study established a three-electrodes system method to investigate charge-transfer and mass-transfer processes of ACFs by electrochemical impedance spectroscopy (EIS). Five commercial ACFs with two different macroscopic surface morphologies and similar specific surface areas were used. The desalination performances of these five ACFs were carried out in a batch mode operated CDI cell under a constant voltage (1.2V). The contact resistances and capacitances of woven ACFs ranged from 5 to 8 Ω and 0.5 to 0.8 μF , respectively. Meanwhile the contact resistances and capacitances of knitted ACFs varied from 10 to 15 Ω and 0.6 to 0.9 μF , respectively. We found that the volumetric capacities of woven ACFs (54.98-58.44 F/cm^3) were larger than that of knitted ACFs (53.73-54.13 F/cm^3). Still, the volumetric adsorption capacities of woven ACFs (2.7-7.1 mg/cm^3) were less than that of knitted ACFs (6.1-6.9 mg/cm^3). In addition, when the macroscopic surface morphologies were the same, volumetric adsorption capacities were positive linearly related to the volumetric capacities. This article provides a simple and easily available approach to measuring the electrochemical properties of ACF via EIS and highlight the importance of macroscopic surface morphology of the porous materials.

Keywords

activated carbon fibers, capacitive deionization, volumetric capacity, volumetric adsorption capacity

P1.79

Investigation of single crystalline Cu₂O films for chemical sensors application

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Abstract

Copper oxide Cu₂O is an important and well-known p-type transition metal oxide semiconductor material which has the advantages of direct band gap 2.1 eV at 300 K, a high absorption coefficient in the visible spectral range. This material has already been employed in the fabrication of electronic devices, thanks to its low cost, non-toxicity and fairly good carrier mobility. For example, Cu₂O has been used in thin photovoltaic devices, resistive switching, transistors, gas sensors or catalysts.

In our work the epitaxial Cu₂O (110) films has been fabricated by Pulsed Laser Deposition on MgO (100) substrates. The oxygen pressure in the chamber was varied between 10⁻³ Pa and 0,1 Pa, while the substrate temperature was between 600 and 770 °C. The crystalline quality and out-of-plane orientation of the films were characterised by means of X-ray diffractometers. The surface morphology was characterised by Atomic Force Microscopy and Scanning electron microscopy. Because we focused on utilization of the Cu₂O films as gas sensors, the powerful technique near ambient pressure photoelectron spectroscopy (NAP-XPS) was carried out to investigation of surfaces of the crystalline films in the presence of gasses and vapours. The idea was to observe the reaction of hydrogen NO_x, ethylalcohol and acetaldehyde on the surface of Cu₂O while exposed to atmosphere as a function of temperature and gas pressure. In parallel the resistance and DC response of the Cu₂O films were in-situ monitored providing information about macroscale processes during gas sensing.

Keywords

chemical sensors, copper oxide

P1.80

Bifunctional hydrogel coatings for urological medical devices

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Abstract

Urological catheterisation is a source of various problems, some of them are injuries and pain, others are nosocomial infections. To solve at least a part of these problems we developed a series of various coatings for urological catheters. To increase biocompatibility and decrease friction coefficient against delicate tissue, coatings are based on the hydrogel-forming crosslinked polyvinylpyrrolidone with various additives, to ensure a proper attachment to the surface of multiple polymers and robustness, proper base coating/surface activation was developed. The first layer is either biocompatible polymer mixtures or polydopamine, which adhere to virtually any surface, including PTFE. The first layer is responsible for adhesion while the second ensures delicate and lubricious contact with tissue. We measured the mass of the coating attached, its stability, and friction coefficients between the coated medical devices and the animal urethra. We compared the results obtained with commercially available urological medical devices with lubricious coatings. The static and dynamic friction coefficients with the urethra for our coating were 0.023 and 0.012, respectively. For the best tested commercial product, these friction coefficients were 0.065 and 0.060, respectively. After five measurements of the same sample, our coating showed a static friction coefficient of 0.056 and a dynamic of 0.023. The same experiment for the best tested commercial product showed friction coefficients of 0.077 and 0.050, respectively. We also added antibacterial agents to our coatings: iodine, triclosan, and octenidine. Disc diffusion test showed strong antibacterial activity against *Staphylococcus epidermidis*, *Escherichia coli*, and *Bacillus subtilis*. These results suggest that our coating can potentially be employed in commercial urological medical devices to reduce the number of infections and tissue injuries during urological surgeries.

Acknowledgements: This work was supported by The National Centre for Research and Development in the frame of 2th joint Polish-South African research projects (contract number: PL-RPA2/05/UROCOAT/2019).

Keywords

hydrogel coatings, antibacterial coatings, lubricious coatings, medical devices

P1.81

Effect of Peptide Secondary Structure and Substrate Charge upon Adsorption at Silica Surface: Modeling and Experiments

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Abstract

Polyelectrolytes (PEs) are charged molecules consisting of ionizable groups, which release counterions when desolating in polar solvents such as water. Recently, polyelectrolytes have been extensively studied due to a number of potential applications in many industrial processes. Especially interesting from the point of view of surface functionalization for medical applications are amino acid-based biomolecules. They are widely used in targeted drug delivery studies, surface functionalization for enzyme and protein immobilization, or biological coatings. Here we present studies on driving forces of peptide adsorption, especially, the influence of the pH on the adsorption process is highlighted. Three different types of molecules were studied namely: poly(L-lysine) (PLL), and poly(L-arginine) (P-Arg) as representatives of polycations, bearing a positive charge under physiological conditions and poly(L-glutamic acid) as a representative of polyanions, bearing a negative charge respectively. Combining experimental techniques, such as laser Doppler velocimetry (LDV), dynamic light scattering (DLS), circular dichroism (CD), quartz crystal microbalance with energy dissipation (QCM-D) and streaming potential measurements, with molecular dynamics simulations (MD modelling) it was revealed that the studied peptides showed pH-responsive adsorption, where electrostatic interactions appeared most dominant in the process of subsequent monolayer formation. Moreover, from MD modelling it was observed that the secondary structure changes upon the adsorption process. Such monolayers can be efficiently used as supporting layers for nanoparticle and protein immobilization.

The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/D/ST5/01866 and Academy of Finland.

Keywords

Peptide adsorption, Molecular dynamics

P1.82

Impedimetric analysis of liquid phase partitioning into the nanoporous copper benzene-1,3,5-tricarboxylate metal organic framework

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Abstract

Impedance spectroscopy provides unique opportunities for the characterization of nanoporous materials with large internal surface areas. Especially nanoporous conductive materials have already been widely studied by impedimetric means for applications such as (electro-)catalysis, capacitive deionization and sensing. By contrast, the application of impedimetric analysis techniques to equally porous dielectrics is still at an early stage.

In this work, we demonstrate a unique characterization strategy which is based on preparing nanoporous dielectrics as a thin film grafted on interdigitated electrode fingers. With the coated electrode chip being placed inside a microfluidic flow cell and contacted to an impedance analyzer, we can study the interaction of the nanoporous dielectric when exposed to different liquids. In case the film thickness is smaller than the effective electric field penetration length of the electrode geometry it is possible to interpret the resulting spectra within the theoretical framework of impedimetric coating science. In particular, a joint evaluation of coating and geometric capacitance provides access to coating thickness and permittivity.

As a first step, we have applied our analysis strategy to the nanoporous copper benzene-1,3,5-tricarboxylate metal organic framework and the resulting change in the impedance signal when it is exposed to ethanolic solution of varying water content. The coating permittivity increases reversibly with an increase in water content which is indicative to the permeation of the internal pores by the liquid phase. In addition, we observe a sharp decrease in coating resistance which is related to the movement of ionic charge carriers through the nanoporous material.

Keywords

Impedance Spectroscopy, Interdigitated Electrodes, Metal Organic Framework

P1.83

Electro-oxidation of dopamine and acid uric using new electrode system based on graphite carbon paste modified with carbon Dots

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Abstract

Dopamine (DO) is an important neurotransmitter, which plays a significant role in the function of human metabolism. It is important to develop sensitive sensor for the determination of DO. The present work deals about the electro-oxidation of DO in presence of acid uric (AU). Thus we developed graphite carbon paste electrode (CPE) having carbon Dots at different proportions, and then they were characterized by different analytical methods (XRD, XPS, SEM, TEM). The electrochemical performance of the new electrode system was studied, and the results were compared with that of commercially existing electrode. The results show that this new electrode has high sensitivity to electro-oxidation of DO even at low concentrations and the presence of AU in the analysis not generate interferences. Interestingly, electrode offers a lower LOD than what has normally been reported before.

Keywords

Dopamine, Electrochemistry , DOTs

P1.84

Environmentally friendly Ni-WC for the dry reforming of waste plastics

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Abstract

Nowadays, waste plastics are a serious environmental problem and new methods for their management is still a concern of world-wide research. Waste plastics subjected to pyrolysis generate gaseous hydrocarbons that can be source of hydrocarbons for the production of syngas via dry reforming. Despite the pro-environmental nature of this process, it is still an industrially immature process due to fast catalyst deactivation. The most widely used catalysts are based on nickel particles, because they have relatively low price and high activity, comparable to the activity of noble metals. However, these catalysts are quickly deactivated due to coke deposition. Transition metal carbides have attracted much interest because of their high thermal stability and catalytic activity. During the DR process, they participate in recarburization-oxidation cycles. This prevents the formation of carbon deposits on the catalyst surface. However, carbides show stable activity only at relatively high pressures. Therefore, combination of both types of catalysts may be an promising alternative to avoid the main constraints associated with the use of catalysts based only on nickel or TMCs. The aim of this research is to develop new catalysts for the DR of waste plastics. Nickel catalysts supported on SiO₂ and MgAl₂O₄ functionalized with nanostructured WC have been proposed. Obtained catalysts were characterized with XRD, XPS, TEM, SEM, BET, H₂-TPR and Raman spectroscopy techniques. The DR of waste plastics were conducted in two-stage fix-bed reactor. The hydrocarbons generated at first stage during pyrolysis were directly transferred to the second stage of reactor filled with catalytic bed for dry reforming. It was found that the type of carbon source strongly affects the physicochemical properties as catalytic activity of obtained catalysts.

Acknowledgment: The financial support for this study from Gdańsk University of Technology by the DEC-23/2020/IDUB/I.3.3 grant under the ARGENTUM—"Excellence Initiative—Research University" program is gratefully acknowledged.

Keywords

dry reforming, waste plastics, transition metal carbides

P1.85

Influence of dopant concentration and annealing on two- and three-phase polymer blends as active materials in OLEDs

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Abstract

Efficient and easy color tuning in organic light emitting diodes (OLEDs) can be achieved by blending polymer semiconductors, which utilize Förster type energy transfer between host and dopants. In order to control the emission profile and operation characteristics of OLEDs is essential to achieve balanced charge transport and efficient energy transfer mechanism. One critical factor is the structural properties of the blends as well as the dispersion of the embedded phases into the host polymer, which determine the extent of the contact and interaction interfaces between the phases. These are defined by the growth processes and parameters, but also by the post-growth annealing treatment. In this work, one-phase films, grown by spin coating technique, by commercial blue Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO), green Poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) and red spiro-copolymer (SPR) light-emitting materials, were initially studied as reference materials. Then, two- and three-phase blends were developed. The characterization of the as grown and annealed films was focused on their optical, photophysical and surface nanotopography properties realized by Spectroscopic Ellipsometry, Photoluminescence and Atomic Force Microscopy, respectively. Following, the fabrication of OLED devices on glass substrates was carried out for the evaluation of blends composition and annealing treatment in terms of devices' functionality. For this purpose, Electroluminescence characterization was carried out to derive the electrical characteristics and electro-emission properties. Their analysis provided insights into the carrier transport and energy transfer mechanisms between the phases, which were correlated to host-guest interactions as well as to the structural changes originated by thermal treatment, which leads to the crystallization of PFO. Finally, it is demonstrated that the photo- and electro-excitation of the as grown and thermally treated blends is markedly differentiated.

Keywords

OLED, polymer blends, Förster energy transfer , Electroluminescence

P1.86

Nickel-modified molybdenum carbide catalysts supported on metal oxides for dry reforming of hydrocarbons from waste plastics

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Abstract

Dry reforming of hydrocarbons (DRH) is an environmentally friendly method for syngas generation due to the utilization of carbon dioxide. The use of waste materials as a source of hydrocarbons in DRH instead of fossil fuels would additionally strengthen its pro-environmental character. Waste plastics seem to be promising and widely available materials as a substrate for syngas production. In the literature, there are reports regarding the possibility of efficient syngas production by pyrolysis of plastics, and then dry reforming of the obtained pyrolysis gases. As catalysts, nickel supported on metal oxides is mainly examined. Nickel catalysts supported on oxides are characterized by high catalytic activity in DRH, however, due to coking and particle sintering, they are quickly deactivated. Metal carbides (MCs) can be an alternative to traditional nickel catalysts. MCs in DRH reaction undergo oxidation-carburization cycles, therefore they are not subject to coking. The combination of carbide and nickel catalysts can allow obtaining highly active and stable catalysts in DRH processes.

In this regard, the presented results refer to synthesis and application of nickel-modified molybdenum carbide catalysts supported on metal oxides for DR of hydrocarbons origin from used plastics. Mo₂C catalysts were obtained with use of various amines as carbon sources and structure-directing agents. The catalysts before and after the process were characterized using XRD, XPS, SEM, TEM, TG, BET surface area, BJH pore size distribution, Raman spectroscopy, H₂-TPR and CO₂-TPD/TPO techniques. Catalytic activity was tested in the DRH formed after plastic pyrolysis. It was found that Mo₂C-based catalysts perform a high activity in DRH and the properties of the used amine had a key role on morphology and thus the catalytic activity.

Acknowledgement: The financial support for this study from Gdańsk University of Technology by the DEC-23/2020/IDUB/I.3.3 grant under the ARGENTUM—"Excellence Initiative—Research University" program is gratefully acknowledged.

Keywords

dry reforming, nickel catalysts, metal carbides, waste plastics

P1.87

Degradation of the dye by heterogeneous Fenton-like reaction using Fe supported over activated carbon prepared from natural and eco-friendly raw materials

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Abstract

Recent studies have revealed that over 1,000,000 tons of organic dyes are estimated to be generated and nearly 15% of the total annual production is lost as industrial wastewater during the manufacturing processes industrial. Most of these dyes are toxic, mutagenic and carcinogenic to both human beings and aquatic life. Therefore, the effective treatment of dye-containing wastewaters with new techniques is necessary and important.

our work reports on the synthesis, immobilization and stabilization of iron (Fe) particles on activated carbon (AC) from date stem material for heterogeneous Fenton-like removal of hazardous pollutants from water.

AC-Fe was synthesized through a simple and sustainable chemical reaction using and resulting in an environment-friendly material.

X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray analysis (EDX) were used to characterize the synthesized samples.

Compared to pure AC, AC-Fe showed higher degradation of toluidine blue O (TBO) dye in aqueous solution. The effects of initial pH, and TBO and H₂O₂ concentrations on TBO degradation were investigated.

The AC-Fe catalyst proved highly efficient in Fenton-like degradation of TBO (50 ppm), with removal of up to 99% in 3 min. This catalyst was used efficiently up to four repeated cycles.

These results prove that date stems – a waste product from agriculture – are a suitable and inexpensive precursor for preparing appropriate AC and catalyst and eliminating dyes from aqueous solution by a heterogeneous Fenton-like reaction.

The above results open an interesting avenue for developing functional green catalysts based on AC-Fe for pollution removal.

Keywords

Catalysis, Activated carbon, Wastewater treatment, surface modification

P1.88

HyStor: Development of novel silica barrier coatings for mitigating H₂ permeation: II – Measurement techniques

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Abstract

With the emerging focus of Hydrogen as a fuel in the Green Economy, there is an urgent need to deliver solutions related to the safe and efficient storage and transmission of Hydrogen. Two critical areas related to both cost efficiency and safety relate to the highly permeable and corrosive properties of Hydrogen molecules as a gas. One area of focus is the formation of barrier coatings to limit both hydrogen permeation and the reduction of its corrosive effects upon the underlying substrate of the storage vessel material. While the formation of barrier coatings as part of the production process of the storage vessels and piping is the primary goal, a secondary goal is to apply such protective coatings in situ within existing infrastructure, such as storage vessels and pipes.

This project will focus on the synthesis and application of novel sol-gel coating materials based on Silica as a flexible approach to deposit Silica network multilayers as cost-effective barrier coatings.

As part of this approach, the process of sol-gel maturation and understanding the forces that drive silica network development and interaction between hydrogen and the newly-developed coated surfaces will be studied dynamically using a range of surface-measurement instruments.

This presentation highlights the key features of the Surface Plasmon Resonance [SPR] and Quartz Crystal Microbalance [QCM] technologies in relation to parallel studies on the chemical composition of the oxide network determined by Raman spectroscopy and structure shown by Scanning Electron Microscopy (SEM).

The research was supported by the National Center for Research and Development in Poland under the Small Grant Scheme (SGS) project 'Improving the Efficiency of Hydrogen Storage Vessels through Novel Oxide Coatings HyStor NOR/SGS/HyStor/0306/2020-00' Programme 'Applied Research' financed through the Norwegian Financial Mechanism

Keywords

surface interaction evaluation, SPR and QCM for oxide structure interaction measurement, thin film, silica sol-gel coating

P1.89

Benefits Of Bifunctional Layers On The Silica Surface For Applying In Adsorption

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Abstract

Silicas of different morphology bearing amino and mercapto groups have been studied for a long time. These moieties, which are often built-in synthetic materials, are usual components of proteins and natural materials and are quite simple and interesting at the same time. Such groups can interact with metals, other organic groups, and molecules, including those of protein nature; thus, they can serve as a support for the formation of multilayer carriers. Silica materials bearing up to 3 mmol/g of amino or thiol groups can be easily produced via a single-stage sol-gel technique. It was shown that the amino groups on the silica particles are usually protonated, and in the absence of other residues possess poor hydrolytic stability or may be unavailable for interactions. Meanwhile, the incorporation of organic residues among 3-aminopropyl groups hinders the access of water molecules and prevents the hydrogen bondings of amino groups with other amino or silanol functions; therefore, amino groups remain stable in aqueous solutions and free to react with adsorbates. The addition of surface hydrocarbon residues or structural organic fragments by means of bridged silanes was also shown to keep 3-mercaptopropyl groups capable of ion-exchange interactions on the surface. Thus, it is possible to point out at least three advantages of bifunctional layers on the surface of silica: (1) different rates of silane hydrolysis enhance the completeness of co-condensation and increase functional groups content compared to monofunctional samples; (2) additional hydrophobic residues along with amino or mercapto groups improve the kinetics of metal ions uptake and increase the sorption capacity of the silica spheres; (3) extra hydrophobic centers ensure the increased adsorption of albumin, urease, or dyes onto the bifunctional samples.

The research was supported by APVV-19-0302, VEGA 2/0156/19, REA No. 734641-NanoMed projects, as well as Swedish Research Council grant DNr.2018-04841.

Keywords

surface chemistry, silica, functional groups, adsorption

P1.90

Asphaltenes – a promising material for adsorption and chromatography

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Abstract

Asphaltenes are a one of four typical groups of hydrocarbons present in crude oil. Generally, these are aromatic-type compounds, defined on the basis of non-solubility in n-alkanes [1]. Asphaltenes quantitatively remain in a residue from vacuum distillation and are a one of important components of bitumens. Due to this reasons and lack – up-till-now - of applicability as pure fraction, asphaltenes can be considered as a low cost material.

Chemical structure of asphaltenes (highly carbonaceous material with high aromaticity and tendency to stacking and formation of graphite-like structure with present functional groups, heteroatoms and metals) makes them an interesting material exhibiting various intermolecular interaction e.g. van der Waals, coulombic, hydrogen bonding or π - π stacking.

This paper presents a summary of several developments of asphaltenes applications in the field of separation techniques. Asphaltenes coated on Chromosorb W-AW-DMCS were effectively used for separation of several volatile organic compounds by gas chromatography [2]. Pristine asphaltenes behaved like semi-polar stationary phase with unexpected very strong interactions with pyridine and its derivatives. While, chemically modified asphaltenes by cyanation or nitration revealed to obtain advantages properties as adsorbents for removal of several compounds from waste gases. Nitrated asphaltenes coated on diatomaceous earth support presented high capacity and strong adsorption making it an interesting alternative to classic activated carbons[3-5]. Performed experiments revealed also their usefulness as catalyst for wastewater treatment by means of persulfate based advanced oxidation processes (AOPs) [6].

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Keywords

asphaltenes, adsorbents, waste gases treatment, wastewater treatment

P1.91

Prediction of adhesive properties of epoxy resin by machine learning approach

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Abstract

In this study, the artificial neural network (ANN) is used to predict the adhesion strength of structural epoxy adhesives. The data sets are obtained by testing the lap shear strength at room temperature and impact peel strength at -40 ° C by the various epoxy adhesive formulation specimens. The linear correlation analysis shows that the content of catalyst, flexibilizer, and curing agent in the epoxy formulation has the highest correlation with the lap shear strength. On the other hand, the epoxy formulation's flexibilizer, promoter, and catalyst content have the highest correlation with the impact peel strength. We constructed the ANN model and optimized it with the selection set and training set divided from the data sets using the analyzed data sets. The optimized ANN model is then verified with test sets divided from the data sets through error and linear regression analysis. The obtained RMSE and R^2 confirm that each model is a suitable predictive model. Therefore, the change of lap shear strength and impact peel strength is predicted according to the change of the content, especially which has shown a high linear correlation with lap shear strength and impact peel strength. Consequently, our prediction model obtains the optimum contents of the formulation components for the optimum adhesive strength of epoxy.

Acknowledgments

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Keywords

epoxy resin, machine learning, artificial neural network, adhesive strength

P1.92

Effect of hybrid thermo-mechanical treatment on the surface properties of biomedical pure Ti with different content of interstitial elements

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Abstract

Nowadays, the demand for long-lasting implants such as dental replacements is extremely high and it continues to grow. Commercially pure Ti (CP-Ti) is widely used in the area of oral implantology. This is associated with the fact that CP-Ti demonstrates the unique combination of low-density, relatively low elastic modulus, high corrosion resistance in body fluids and biocompatibility. However, the mechanical strength of CP-Ti is too low to use this material in the load-bearing applications such as modern narrow dental implants. One of the possible ways to overcome this drawback is grain boundary and dislocation strengthening by large plastic deformation methods. The advantageous mechanical properties of plastically-deformed Ti can be further enhanced by low-temperature heat treatment. Introduction of crystal lattice defects (grain boundary/dislocations), and their rearrangement during low-temperature annealing, can influence the properties of protective oxide layers and thereby electrochemical response of CP-Ti biomaterial. Moreover, resultant corrosion resistance can be influenced by CP-Ti purity, precisely the content of interstitial elements. Thereby, the aim of this study is to gain knowledge about the effect of density and character of crystal lattice defects on the corrosion resistance of CP-Ti with different amounts of interstitial elements. Corrosion performance was verified by electrochemical tests (EIS, potentiostatic polarization, Mott-Schottky measurements) carried out in artificial saliva enriched with fluoride ions, which are present in commonly used products for oral hygiene. Electrochemical tests were supplemented by analysis of microstructure (TEM/STEM), surface morphology (SEM, optical profilometry), and surface chemical composition (XPS) of tested materials.

This work was supported by The National Science Centre Poland [Grant number 2018/29/B/ST8/02883].

Keywords

titanium, biomaterials, Electrochemical tests, Surface analysis

P1.93

Zeolitic Imidazolate Framework-67 Based Electrode For Efficient Capacitive Deionization

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Abstract

Capacitive deionization (CDI) is an emerging and environmentally friendly technology for water desalination with promising future. The electrode material with high electrosorption performance is critical in CDI application. Here, we report the synthesis and study of porous carbon derived from zeolitic imidazolate framework-67 (ZIF-67) for electrosorption study of NaCl. The morphology and graphitic degree are analysed by X-ray diffraction, Raman spectroscopy and scanning electron microscope. The electrochemical analysis is performed using cyclic voltammetry and galvanostatic charge-discharge confirming the significant increase in the specific capacitance of porous carbon derived from ZIF-67. Further, the porous carbon derived from ZIF-67 was studied for deionization of water and exhibits high electrosorption capacity of 28.13 mg/g for initial salt concentration of 800 mg/L at 1.4 V.

Keywords

Capacitive deionization, Metal organic frameworks, ZIF-67, Electrosorption Capacity

P1.94

Cu₂O-coated copper nanopillars for photocatalytic water cleaning

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Abstract

Water pollution is a severe problem in many parts of the world. In developed countries the increased use of chemicals and urban densification has started to cause stress of previously well-functioning water systems. Advanced oxidation processes (AOPs), is a promising method for degradation of artificial organic pollutants, which are challenging to remove by conventional water treatment techniques. In AOPs hydroxyl radicals (OH•) and reactive oxygen species (O₂⁻ and O₂²⁻) which are strongly oxidizing species are generated and these subsequently react with and degrade the pollutants. To use nanostructures which are optically active in the visible part of the spectrum is attractive because it both creates a large surface area, promoting surface interface reactions, as well as enables the utilization of a large part of the solar spectrum. In this study flat copper surfaces and 3D nanostructured copper pillars are utilized as base structures. These are subjected to thermal oxidation at low temperature, for a controlled amount of time, creating thin copper oxide layers which makes them photoactive in the visible range. The formed copper oxide and its growth is analysed with SEM, XRD and Raman spectroscopy, and show the formation of Cu₂O with a slight incorporation of CuO for the thickest oxide layers. Formation of CuO nano needles, protruding from the Cu₂O layer, were observed in the SEM imaging. The photocatalytic performance was tested by degradation of methylene blue in aqueous solution and all of the tested systems showed quite effective performance. The highest degradation rate was seen for copper nanopillars annealed for 4 or 8 min, which exhibited 34% faster degradation than the oxidized flat sample. The study shows that simple and inexpensive thermal oxidation processes can be used to create efficient photoactive Cu₂O catalysts even on semi-flat surfaces, and that nanostructuring increases the degradation rates.

Keywords

Photocatalysis, Cu₂O, Nanostructures, Water cleaning

P1.95

Assessment of surface texture quality of casting models produced with selected 3D printing technologies

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Abstract

The dynamic development of unconventional manufacturing technologies, in particular 3D printing technology, opens up new manufacturing possibilities for designers and technologies. This applies to the production of final models as well as semi-finished products and tools for further production processes. The ongoing industrial revolution 4.0 entering a dynamic phase means that additive technologies are more and more used in new industrial sectors. The application of 3D printing technology in the foundry industry that is one of the promising innovations of the last few years, which can significantly accelerate the casting process. In these cases, 3D printing can be used both for the construction of foundry models and for the production of ready-made molds. It seems, however, that the production of casting models with the use of 3D printing technology, due to the lower price compared to making foundry molds with additive technologies, is the easiest way to implement 3D printing in the foundry industry.

The presented paper presents the results of research carried out as part of the "*Lider*" project of the National Centre for Research and Development, whose main goal is to assess the mechanical, metrological and tribological properties of casting models produced with 3D printing technologies. Three additive technologies were used for the research: Selective Laser Sintering, Photo-curing of Liquid Polymer Resins, and Fused Deposition Modeling. The study analyzes the influence of technological parameters such as the printing direction, the layer thickness, or the process parameters of the SLS laser on the surface texture quality of foundry models analyze by profile and surface parameters. It has been clearly demonstrated that the printing direction is a key parameter influencing the surface quality of the samples produced and that the appropriate adjustment of the laser power and speed allows for control surface quality and in some cases increasing the strength.

Keywords

3d printing, casting, SLS, PJM

P1.96

Surface waviness of casting patterns manufactured by selected 3D printing technologies

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Abstract

The dynamic development of the foundry industry requires the implementation of modern manufacturing methods to produce foundry patterns and casting molds. Additive technologies (3D printers) can be successfully used for this purpose. Today 3D printers allow the production of fully functional parts without the need for further processing. The application of 3D printers significantly improves the process of producing foundry patterns in comparison to traditional methods of their production. It should be noted that the quality of the surface texture of the foundry pattern is crucial because it affects the quality of the casting mold and finally affects the finished casting. Therefore, it is necessary to select the appropriate technological parameters of 3D printing in such a way as to obtain foundry patterns with high strength and the appropriate quality of the surface layer. In most studies, the surface texture is examined by analyzing the 2D or 3D roughness parameters. This is a certain limitation because, in the case of 3D printing, the influence of technological parameters is more visible for unevenness of a longer range, such as surface waviness.

In the paper, the influence of the basic technological parameters of 3D printing on the formation of the waviness of the surface of foundry models has been analyzed. Three different 3D printers in terms of printing technology and building material were tested: PJM (PolyJet Matrix) FDM (Fused Deposition Modeling), SLS (Selective Laser Sintering). In addition, the surfaces waviness of models manufactured with traditional methods were analyzed. The preliminary results of the research showed that the printing direction significantly influences the values of the waviness parameters of the surface of the foundry patterns made with FDM, PJM, and SLS additive technologies.

Keywords

surface waviness, 3D printing, additive technologies , topography

P1.97

An insight on fragmentation process of plastic materials by XPS analysis

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Abstract

Plastics are synthetic organic materials, characterized by a high degree of chemical resistance, considerable plasticity as well as the versatility of performance and ease of processing. All these properties have led to the immoderate use of plastic materials with their subsequent release into the natural environment, due to the mismanagement at the end of their life cycle and their poor biodegradability. Despite their resilience and resistance, plastics can undergo fragmentation processes by physical-chemical and biological agents, producing microplastics (MPs) or even nanoplastics (NPs). However, determining their fate is inherently difficult, both because the timescale of degradation and the dynamics of these processes are not clear and grey areas remain. The application of a surface technique like X-ray Photoelectron Spectroscopy (XPS) can be of great importance in disclosing fragmentation mechanisms.

It is well known that the fragmentation process originates from the oxidation/hydrolysis of plastic materials. These processes can be monitored by XPS as they lead to the modification of C 1s (and O 1s) signals by the appearance/increase of components attributable to chemical moieties such as hydroxyl, carbonyl and carbon-oxygen functionalities. In this work, we propose the use of the XPS technique, for chemical characterization of different types of plastic materials: polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS), polyethylene (PE), before and after a series of treatments aiming at simulating environmental conditions determining oxidation/hydrolysis processes, in order to understand which processes, play a major role in plastics modifications towards fragmentation. In brief, plastic standard samples are artificially weathered for different time intervals under experimental conditions including exposure to controlled UV radiation/darkness, and water/hydrogen peroxide solution (Figure 1).

After each treatment, the plastic standard samples are filtered using glass microfiber filters and then analyzed by XPS to identify and quantify chemical groups generated.

Keywords

plastics, fragmentation, XPS, surface characterization

P2.01

Removal of pharmaceuticals by phosphorus and sulfur co-doped graphitic carbon nitride incorporated into 2D TiO₂

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Abstract

Solar-driven photocatalysts are considered green materials since their absorbance response corresponds to solar light wavelength, and the sunlight is a sustainable and renewable energy source.

In the present study, a novel 2D TiO₂-based hybrid photocatalysts with enhanced photocatalytic activity under UV-vis light were prepared by heterojunction of layered TiO₂ obtained by simple lyophilization method with multi-anion doped g-C₃N₄. In order to improve the properties of the 2D TiO₂/g-C₃N₄ composite, organic precursors of phosphorus and sulfur were introduced into the structure of g-C₃N₄. The addition of sulfur in the g-C₃N₄ increased the porosity of the surface since it homogeneously substitutes the lattice nitrogen (N) with sulfur (S), while the addition of phosphorus (P) increased the separation efficiency of photogenerated electrons and holes and lowered the bandgap energy.

Herein, a type II heterojunction multi-anion doped g-C₃N₄/ 2D TiO₂ composite is proven to be an efficient photocatalyst for solar-driven degradation of emerging pollutants from the group of pharmaceuticals not susceptible to biodegradation. For carbamazepine, about 100% degradation was achieved within 30 min of photodegradation, whereas for acetaminophen, the complete removal was observed in 120 min of irradiation under simulated solar light. Moreover, the mineralization efficiency measured as TOC values was 76% for carbamazepine and almost 40% for acetaminophen.

The photoluminescence spectra and carriers' lifetime calculations showed better separation of charge carriers in UV light for 2D TiO₂ and under 405 nm excitation (absorption maximum of (P, S)-g-C₃N₄ and sideband of (P, S)-g-C₃N₄/TiO₂ for the composite material. The responsible species for the degradation of pharmaceuticals were superoxide (O₂^{•-}) and hydroxyl radicals (HO[•]), which contributed to the complete photodegradation of studied pharmaceuticals belonging to the group of persistent organic pollutants.

Acknowledgments

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Keywords

2D TiO₂, g-C₃N₄, pharmaceuticals degradation, photocatalysis

P2.02

Disposable screen-printed electrode containing graphene oxide with three-dimensional architecture for the determination of ascorbic acid in fruit juices

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Abstract

In this work, a screen-printed disposable electrode was used as a substrate for the development of a three-dimensional sandwich-type graphene oxide architecture through three simple steps of electrodeposition. Firstly, GO was reduced on the SPE surface (SPE/GO). Second, zinc nanoparticles (ZnNPs) were deposited on the SPE/GO surface to obtain the SPE/GO-ZnNPs electrode. Then, another layer of GO was electrodeposited on the electrode to form a sandwich-like surface (GO-ZnNPs-GO). Finally, the ZnNPs were electrolyzed from the electrode surface to obtain a GO surface with three-dimensional aspects (SPE/3D-GO). The modified electrode was characterized by scanning electron microscopy, Raman spectroscopy, Fourier-transform infrared spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. The proposed electrode was used for the electrooxidation of ascorbic acid by linear sweep voltammetry. Under optimized conditions, ascorbic acid presented an intense oxidation peak at -0.10 V on the SPE/3D-GO electrode. The current peak of ascorbic acid oxidation was linearly proportional to the concentration in the range of 1.0×10^{-5} to 0.01 mol L⁻¹, with a detection limit of 3.4×10^{-6} mol L⁻¹. In addition, the proposed electrode showed excellent selectivity, reproducibility and stability. As a proof of concept, the SPE/3D-GO electrode was successfully applied for the determination of ascorbic acid in orange and grape juices. The amount of ascorbic acid found in the orange and grape juice samples was 1.2×10^{-3} and 6.1×10^{-4} mol L⁻¹, respectively. The proposed electrode showed recovery values between 99 and 105%, with RSD values $\leq 4.3\%$. These results indicate that the electrode developed can be applied for monitoring ascorbic acid in fruit juices.

Acknowledgements

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Keywords

Screen-printed electrode , Three-dimensional graphene oxide, Ascorbic acid , Fruit juices

P2.03

Bioadhesive behavior of poloxamer/hyaluronic acid-based formulations analyzed by rheology method

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Abstract

Systems based on Poloxamer and hyaluronic acid have been developed for treatment of back pain as drug delivery formulations. Due that, it is important to study interactions among components and their ability to adhere to mucosa, since these formulations can release drugs on the target. Aqueous formulations with Poloxamer (PL) 407 15 %, 30% (w/w), and binary system PL 407 15% + PL 338 15%, with hyaluronic acid (a very hydrophilic polymer) at 0.5% (w/w) and the anesthetic bupivacaine (5 mg/mL). To simulate mucosa, it was prepared mucin solutions. The bioadhesive force (F) was obtained from the relation $F = \sigma \eta_b$, where η_b is viscosity component due to biodhesion, and σ is shear stress obtained from curve flow of each formulation. Moreover, to analyze the role of each component of all formulations, the relative rheological synergism ($\Delta G'/G'$) was obtained from experimental data at 1 Hz. It is pointed that binary systems show augmented ability to adhere to mucin, approximately 1000 times higher than other formulations. When it added hyaluronic acid to PL 407 15 % and binary system, it is observed the adhesion force increases twice, indicating that hydrogen bonds between HA chains and mucin components are formed. The role of more hydrophilic polymers (such as PL 338 and HA) in the interaction between the formulation and mucin is evidenced in the $\Delta G'/G'$ results, where it is seen the interaction between PL 407 15% + PL 338 15% and mucin is almost 20 times greater than PL 407 30%, and the addition of HA to PL 407 30% enhances the effect almost 10 times than in its system alone. This work intends to show that the design of formulations of pharmacological interest can be favored with the use of simple models.

Keywords

Drug delivery, Rheology, Bioadhesion, Mucoadhesion

P2.04

Poly-L-arginine molecule characteristics in simple electrolytes: experiments and molecular dynamic modeling

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Abstract

Among various macroions, poly-L-arginine (P-Arg) is especially attractive. It represents a group of cationic biopolymer composed of physiologically active L-arginine aminoacid. P-Arg molecules have been extensively studied as drug nanocarriers, a component of multilayers for wound healing dressings, as an antibacterial and antimicrobial agent, anticancer vaccines etc. Even though the interactions of P-Arg molecules with other macroions and surfaces depend on various physicochemical parameters such as: molar mass, specific density, size, geometry and surface charge, few investigations were carried out focused on thorough physicochemical characteristics of molecules in electrolyte solutions. Here we present the studies comprising physicochemical properties of P-Arg molecules in NaCl solutions determined by Molecular Dynamics (MD) modeling and various experimental techniques. Primarily, the molecule conformations, the monomer length and the chain diameter were theoretically calculated. These results were used to interpret experimental data, which comprised the molecule secondary structure (CD measurements), the diffusion coefficient and the hydrodynamic diameter (DLS measurements) and the electrophoretic mobility (LDV measurements) determined at various ionic strengths and pHs. Using these data, the electrokinetic charge and the effective ionization degree of P-Arg molecules were determined. In addition, the dynamic viscosity measurements for dilute P-Arg solutions allowed to determine the molecule intrinsic viscosity, which was equal to 500 and 90 for ionic strength of 10^{-5} and 0.15 M, respectively. This confirmed that P-Arg molecules assume extended conformations and approached the slender body limit at the low range of ionic strength. The experimental data also enabled to determine the molecule length and the chain diameter, which agreed with theoretical predictions. Exploiting these results, a robust method for determining the molar mass of P-Arg samples, the molecule hydrodynamic diameter, the hydrodynamic diameter, the radius of gyration and the sedimentation coefficient was proposed.

The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/D/ST5/01866.

Keywords

P-Arg molecules in NaCl solution, molar mass, specific density, size, geometry and surface charge of macroions, CD, DLS, LDV, viscosity measurements, conformation of P-Arg molecules in electrolyte solutions

P2.05

Revealing the adsorption mechanisms of poly-L-lysine at solid/liquid interfaces using electrokinetic techniques and theoretical modelling

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Abstract

Efficient adsorption of polypeptides at solid substrates is of continuous interest for designing biologically active surfaces. Despite of extensive experimental effort, the fundamental physicochemical properties of PLL molecules in aqueous solutions, affecting the adsorption processes, remain largely unknown. To fill up this gap, thorough physicochemical characteristics of PLL in electrolyte solutions was performed, using complementary experimental techniques such as micro-electrophoresis, dynamic light scattering, and viscosity measurements. Using these techniques and the molecular dynamics modeling, molecule density, the chain diameter, the monomer length and the cross-section area in the side-on orientation were determined for the first time. It is worth underlying that the role of the pH has been systematically evaluated in our measurements, especially, the effective electrokinetic charge of PLL molecules in bulk and their monolayers under various conditions. The studies also revealed narrow pH range at which the molecules are charged enough to form a stable colloidal suspension but maintaining their α -helix content above 60%; an elevated charge state of the peptides that is required for colloidal stability promotes the peptide solvation as a random coil. Afterward, the PLL adsorption kinetics on solid substrates was derived from the random sequential adsorption (RSA), and the streaming potential method. The experimental data were successfully interpreted in terms of 3D electrokinetic model, which confirmed the side-on adsorption of PLL molecules on the surface with the fraction of side-on with crossing adsorption for the coverage above 0.3. Additionally, using this method, the stability of the monolayers, evaluated via desorption kinetic measurements, was determined. It was shown that PLL molecules adsorbed in the side-on conformation remain irreversibly bound with the surface. Such stable PLL monolayers can be efficiently used as supporting layers for protein immobilization.

The study was supported by the National Science Centre Research Grant Sonata, UMO 2018/31/D/ST5/01866 and Academy of Finland.

Keywords

physicochemical properties of PLL molecules, adsorption of PLL at solid/liquid interfaces, Streaming potential of PLL adsorption, Stability of PLL monolayers

P2.06

Surface engineering of steel biomaterials by deposition of graphene flakes

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Abstract

The graphene family nanomaterials are an exciting promise in biomedical applications such as tissue engineering, bone regeneration, stem cells differentiation, and bio-imaging. The specific properties of graphene-based biomaterials, which play a pivotal role in regenerative medicine applications include electrical conductivity, good mechanical properties, large surface area, and tunable surface functionalities. The major issue concerning the use of graphene-based biomaterials is the infection risk and subsequent complications causing additional treatment and higher mortality. The study aimed to evaluate the structural and microbiological properties of the surface of stainless steel SS316L coated with graphene flakes. The investigations were focused on the initial step of bacteria colonization, which is crucial for infection and biofilm formation on implant surfaces.

In this work, we have investigated the effect of the functionalization of SS316L surfaces with graphene flakes on electronic properties, wettability, and bacterial adhesion. The investigated samples were thoroughly characterized by RS, XPS, SEM, AFM, contact angle, work function measurements, and bacterial adhesion tests. The bacterial adhesion was evaluated for a series of pathogenic microorganisms, which are responsible for biomaterials associated infections (BAI) i.e., *Staphylococcus epidermidis*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*.

it was found that the obtained graphene coating is mechanically and hydrolytically stable on the surface of stainless steel. Additionally, the application of graphene flakes results in increasing wettability of the surface and work function value. The obtained results were discussed in terms of corrosion inhibition, quenching of heavy metal ions release, biocompatibility and risk of infection.

This study was supported by the National Science Centre, Poland, under grants no 2020/37/B/ST5/03451

Keywords

graphene, biomaterials, corrosion, biocompatibility

P2.07

Hybrid functionalization of spherical silica particles by graphene oxide and octadecylsilane applied to the chromatographic analysis of human biomarkers

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Abstract

Graphene and graphene derivatives have found applications in many fields of science. In antithetical chemistry, it is no different. Graphene derivatives are being applied in sensors, sampling preparation, chromatography, and others. Due to the high surface area of the graphene oxide sheets, this compound became attractive to the production of liquid chromatography columns. Recently, the CROMA group has published a series of articles demonstrating the viability of graphene-derived materials as the stationary phase for extraction columns on bidimensional column-switching chromatography. This work presents the application of hybrid functionalized spherical silica particles by graphene oxide and octadecylsilane as a stationary phase of analytical columns for the separation of hormones. The chromatography performance of different particles diameters is compared, and an explanation based on the surface characteristics of each material is presented.

Keywords

HPLC, Graphene-oxide, Hybrid particles, Capillary LC

P2.08

Optical and electrical study of amorphous titanium oxide thin films derived by reactive spark ablation

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Abstract

Developing an easy, low cost method of titanium oxide thin film preparation has been of significant importance in the last decade as they show beneficial functional properties such as good transparency, thermally activated conductivity, wide bandgap and low work function making them suitable for photovoltaic devices, transistors, sensors, etc. [1]. Here we report on the potential use of reactive spark ablation, a novel, low cost and clean method, to produce amorphous titanium oxide thin films suitable for optoelectronic applications by fine tuning the deposition parameters. All of the deposited thin films were characterized at synchrotron X-ray diffraction beamline, also by AFM and SEM which confirmed amorphous structural organisation and meso-nanoporous morphology. XPS spectroscopy was used to determine the Ti:O ratio, while optical bandgap and temperature dependent conductivity were obtained by DRS and electrical measurements using an electrometer.

Keywords

titanium oxide, spark ablation, solar cells

P2.09

A novel zwitterionic Graphene oxide/Poly(vinylimidazole) material as an adsorbent for the removal of gold ions from aqueous solutions and a catalytic for the A₃ coupling

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Abstract

In this study, we have designed a novel multi-functional zwitterionic GO-based adsorbent for high-efficiency removal of AuCl₄⁻ ions from aqueous solutions and displaying a catalytic activity for the A₃ coupling. First, the functionalization of graphene oxide (GO) sheets by allylamine (Ally) was followed by *in-situ* polymerization of vinylimidazolium (Vim) onto the GO-Ally surface. Then, the zwitterionic [GO-Ally-PolyVim-PS] material was obtained by grafting of 1,4-propanesultone onto the GO-Ally-PolyVim surface. The characterization of the zwitterionic GO-based material was investigated by Fourier transform infrared (FT-IR), Scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA). Then, the adsorption behavior of zwitterionic [GO-Ally-PolyVim-PS] towards AuCl₄⁻ ions was studied as a function of the pH value and the contact time. In addition, to examine the mechanism of the adsorption process, pseudo-first, pseudo-second-order and intraparticle diffusion models were fitted to experimental kinetic data. It was shown that the pseudo-second-order model was appropriated to describe the AuCl₄⁻ ions and the spontaneous reduction of AuCl₄⁻ ions on the surface of zwitterionic [GO-Ally-PolyVim-PS] allowed the formation of gold nanoparticles (AuNPs). In addition, we studied the activity of [GO-Ally-PolyVim-PS]@AuNPs supported as a catalyst for the A₃ coupling of aldehydes, amines, and alkynes through C-H activation under green experimental conditions. Importantly, the heterogeneous catalyst [GO-Ally-PolyVim-PS]@AuNPs was consecutively recycled ten times without any loss of its activity.

Keywords

Graphene oxide sheets, Polymerization, Removal of AuCl₄⁻ ions, Catalytic activity

P2.10

Thermal behaviour of epoxy resin coating modified with granite powder waste

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Abstract

Industrial floors are often finished with epoxy resin coating because of its high chemical resistance. However, the components used to prepare the floor surface are aggressive and hazardous to human live and environment. Moreover, the epoxy resin has poor durability when it is exposed to temperature above its glass transition temperature. To create more environmental-friendly coating and change its thermal properties authors decided to modify epoxy resin with granite powder to reduce use of chemicals. The powder is waste sourced from mechanical treatment of granite blocks during extraction and preparation to export. Thousand metric tons are stored and not used. The problem is serious and visible in countries which extract this material. Application of the waste in epoxy resin coating instead of standard filler could reduce extraction of raw material (quartz sand). Furthermore, low powder size (up to 0.14 mm) perfectly fit to coating thickness (coating has mostly from 1 to 3 mm). Differential scanning calorimetry was used to analyse thermal properties of specimens. A few specimens of coating were modified with different content of granite powder. The specimen with the highest content of granite powder was designed to obtain consistency which can be easily applicated on site to create self-levelling floor surface. During the studies the temperature increment was various to see how it affects the results. Also, the rapid temperature change was applied to simulate thermal shock load (the next serious problem of polymer surfaces). The preliminary results show that modification of epoxy resin coating with granite powder waste has positive influence on thermal properties of composite. Also, created material is more environmental-friendly what is even more beneficial.

Keywords

epoxy resin coating, granite powder, waste, thermal properties

P2.11

Functionalization of SBA-15 mesoporous silica with amine and thiol for highly efficient adsorption of glutathione from aqueous solutions: characterization and modeling studies.

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Abstract

SBA-15 mesoporous materials were prepared using an amphiphilic triblock copolymer (P123) as a template and tetraethylorthosilicate (TEOS) as a silica source under in acidic medium according to the method described by [1]. Then, the materials were functionalized with either 3-(aminopropyl)triethoxysilane (APTS) or 3-mercaptopropyl)triethoxysilane (MPTMS) in order to introduce amine or thiol groups onto the surface by using a post-grafting method. The functionalized materials (SBA-15-NH₂ and SBA-15-SH, respectively) were characterized by FTIR, TGA, XPS, SEM and TEM. Then, the as-prepared materials were used as adsorbent for the adsorption of glutathione (GSH) molecules from aqueous solutions. Nevertheless, the adsorption capacities of glutathione (GSH) molecules of the SBA-15-based materials were studied after each step and it was shown that the contact time and the initial GSH concentration significantly affect their adsorption capacities. In particular, it was shown that the maximum adsorption capacities of the SBA-15-NH₂ adsorbent were as high as $1.940 \pm 0.054 \text{ mmol.g}^{-1}$ for GSH molecules under optimal experimental conditions (GSH concentration=10 mg.L⁻¹, pH=7 and T=293 K). To examine the underlying mechanism of the adsorption process, pseudo first order, pseudo-second order, Elovich, Aharoni, interparticle diffusion models were fitted to experimental kinetic data. It was shown that the pseudo-second-order model was appropriate to describe the adsorption of GSH molecules by SBA-15-SH and SBA-15-NH₂ solid materials. Furthermore, the Freundlich, Langmuir and Harkin-Jura approaches analyzed adsorption data. Moreover, adsorption thermodynamics of GSH molecules have been studied at various temperatures and confirmed the endothermic adsorption nature of the adsorption process onto the SBA-15-SH adsorbent.

Keywords

SBA-15 material, Characterization, Adsorption, Modeling

P2.12

Graphene modified “black {001}TiO₂” nanosheets for removal of ethylene: an operando DRIFTS approach

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Abstract

Ethylene is a natural plant hormone that accelerates the senescence and ripening of fruits during the postharvest period. The quality of fruits become severely damaged at ethylene levels higher than 0.10 $\mu\text{L L}^{-1}$ in fruit storage areas. Therefore, preventing the action of ethylene from the atmosphere surrounding ethylene-sensitive fresh products is one of the main challenges in the development of new postharvest technologies. In this work, the removal of ethylene in absence and in the presence of humidity is assessed using rGO modified anatase {001} black TiO₂ nanosheets (rGO-B-TiO₂ NSTs). The rGO-B-TiO₂ NSTs were synthesized through a simple solvothermal and solid state reaction. Crystal facets, surface sites, size and shape of the synthesized materials were characterized using the XRD, Raman, and HR-TEM analyses, respectively. The synthesized nanosheets of rGO-B-TiO₂ exhibit a high surface area (284 $\text{m}^2 \text{g}^{-1}$) where ethylene adsorption takes place in the absence (48 mmol g^{-1}) and in the presence of humidity (34 mmol g^{-1}). During adsorption experiments, DRIFTS in mode operando allows identifying the chemical surface interactions of ethylene molecules with active surface sites of rGO-B-TiO₂ NSTs. Ethylene molecules seems to be chemisorbed over the rGO-B-TiO₂ NSTs through hydrogen bonding, π - π interaction and di- σ -bonded interactions, respectively. Moreover, the presence of humidity on the surface of rGO-B-TiO₂ NSTs competes with ethylene, predominantly occupying the hydroxyl sites like $\text{H}_2\text{O}\cdots\text{HO-Ti}$, $\{\text{HOH}\cdots\text{O(H)-Ti}\}$. In spite of the fact that humidity affects ethylene adsorption capacity, rGO-B-TiO₂ NSTs are able to remove ethylene through the virtue of π - π and di- σ -bonded interactions even at high relative humidity. The obtained results suggest that rGO modified {001} black TiO₂ NSTs could be used for effective removal of ethylene from high-volume of fruit storage rooms.

Keywords

Adsorption, Ethylene, DRIFTS operando, Modified graphene oxide

P2.13

Wettability of graphenic surfaces: experiments supported by theoretical modeling

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Abstract

Graphene has gained global interest in the fields of science, physics, chemistry and biomedicine due to its extraordinary electrical, optical and mechanical properties. Graphene-based 2D materials are investigated intensively for their biocompatibility and antibacterial properties demonstrating their potential in biomedical applications. The major issue with graphenic surfaces is their chemical inertness and hydrophobic nature that leads to poor wettability and biocompatibility. This problem can be resolved by surface functionalization with polar oxygen functional groups.

The aim of this work was to investigate the modification of the graphenic surface by oxygen plasma treatment in order to enhance its hydrophilicity. The graphenic surfaces were treated via oxygen plasma (25-100 W, 0.2 mbar, 6-300 s). The materials were thoroughly characterized (SEM, XPS, TG/DTA, Raman spectroscopy) while the wettability was probed by water contact angle measurements. The experiments were supported by theoretical calculations using Lorf-Klinowski-type models of oxygen-modified graphene (DFT+D). It was observed that the introduction of the oxygen group modifies the wettability of the surface by decreasing the WCA from 100° to 5°. Moreover, SEM images, TG/DTA data and Raman spectra, confirmed no significant changes in morphology and bulk structure, indicating, however, that the modifications are limited to the outmost surface. The trend in WCA changes upon oxygen functionalization was discussed in terms of the molecular model where the adhesion changes were determined computationally.

This study was supported by the National Science Centre, Poland, under grants no. 2020/37/B/ST5/03451

Keywords

DFT calculations, Water contact angle, Plasma treatment, Wettability

P2.14

CZA catalysts modifications for improvement of dimethyl ether synthesis in laboratory and model scale

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Abstract

Dimethyl ether (DME) is known as potential modern fuel. It possess performance properties similar to LPG, however, due to the lack of a carbon-carbon bond it burns without emitting solid particles which makes it environmentally friendly.

DME can be produced by the direct and indirect method. The indirect method consists methanol synthesis and its dehydration in two separate steps, while direct synthesis involves both operations in one step. The direct process, which is still at the development stage, allows to reduce both investment costs and production costs. The limiting factor is use of an appropriate catalyst that enables high process efficiency, long service life, relatively low price and easy regenerability. The catalyst used for DME synthesis is bifunctional catalyst composed of metallic and solid acid parts for methanol synthesis and dehydration, respectively. The most widely used catalysts are based on copper, Zincium and Alluminium oxides and zeolite dehydration part. These catalysts are quickly deactivated under the conditions of DME synthesis, therefore it is necessary to search for new catalysts or modify the currently used.

In this regard, the presented results refer to the synthesis and application of metal modified (Zr, Fe, Ba, Mg, Li) CZA catalysts combined with Al₂O₃ for direct DME synthesis. The catalysts before and after the process were characterized using XRD, TEM, TG, BET surface area, BJH pore size distribution, NH₃-TPR and O₂-TPO techniques. Catalytic activity was tested in the one step DME synthesis in pressurized slurry bed reactor. It was found type and amount of used modified metal determined the morphology, activity and stability of bifunctional catalyst.

This research was co-funded by National Centre of Research and Development and Polskie Górnictwo Naftowe i Gazownictwo SA in the EU Smart Growth Operational Programme, grant number POIR.04.01.01-00-0064/18-00.

Keywords

catalyst, synthesis, CZA, dimethyl ether

P2.15

The influence of the sealing process on the surface properties of anodized AlSiCu alloys

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Abstract

The sealing process is one of the final steps of the anodizing process where the microporosity of the oxide layer is sealed to avoid the penetration of aggressive substances and to increase the corrosion resistance of the substrate. This treatment influences also the mechanical proprieties of the surface; the hardness and the wear resistance of the oxide layer are affected by the type of sealing process. In this work, the effects of hydrothermal and cold sealing processes on the mechanical proprieties of the anodic layer have been studied. High-pressure die-cast AlSi9Cu3(Fe) alloy plates were anodized in a sulfuric acid electrolyte at 16°C and further sealed in boiled water or in a NiF₂ solution at 25°C. Microhardness measurements, as well as wear and scratch tests, were performed to characterize the mechanical proprieties of the oxide layer. A Pulstec μ-X360s X-ray analyser was used to measure the residual stresses induced by the sealing process. The results report the evolution of the surface proprieties at different steps of the anodizing process. The surface resistance of the oxide layer was quantified in terms of material loss and hardness.

Keywords

Anodizing, AlSiCu alloy, Surface proprieties, Residual stresses

P2.16

Synergistic effect of screen-printed single-walled carbon nanotubes and phosphorylated cellulose nanofibrils on thermophysiological comfort, thermal/UV resistance and electroconductive properties of FR fabric

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Abstract

Single-walled carbon nanotubes (SWCNTs) and phosphorylated nanocellulose fibrils (PCNFs) were used as functional screen-print coatings on flame-retardant (FR) fabric, to further improve its thermal resistance and thermophysiological comfort (wetting, water vapour and heat transmission) properties, while inducing it with electrical conductivity and UV protection. The effect of PCNF printing, followed by applying a hydrophobic polyacrylate (AP), on the same (back/B, turned outwards) or other (front/F, turned towards skin) side of the fabric, with and without the addition of 0.1–0.4 wt% SWCNTs, was studied by determining the amount of applied coating and its distribution (microscopic imaging), and measuring the fabric's colour, air permeability, thickness and mass change.

A both-sided printed fabric (front-side printed with PCNF and backside with SWCNTs within AP) resulted in an increased heat transfer (25%) and an improved thermal resistance (shift of degradation temperature by up to 18 °C towards a higher value) and UV protection (UPF of 109) without changing the colour of the fabric. Such treatment also affected the moisture management properties with an increased water-vapour transfer (17%), reduced water uptake (39%) and asymmetric wettability due to the hydrophilic front (Contact Angle 46°) and hydrophobic back (129°) side. A pressure-sensing electrical conductivity (up to $4.9 \cdot 10^{-4}$ S/cm with an increase to $12.0 \cdot 10^{-4}$ S/cm at 2 bars) of the SWCNT-printed side ranks the fabric among the antistatic, electrostatic discharge (ESD) or electromagnetic interference (EMI) shielding protectives.

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Keywords

SWCNT, Phosphorylated nanocellulose, Fabric screen-printing, Thermal/UV resistance and electroconductivity

P2.17

Hyaluronan-engineered core–shell nanoassemblies for synergistic cancer therapy via a cascade of ROS generation and autophagy inhibition

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Abstract

Blocking autophagy can increase the sensitivity of tumor cells to anti-tumor drugs and improve the efficacy of anti-tumor therapy. As a signal molecule, ROS induces autophagy through various mechanisms. ROS produced by photodynamic therapy can induce cell apoptosis or death in the locally irradiated area. The majority of ROS (about 90%) in cells come from mitochondria, and the level of GSH expression in mitochondria of tumor cells (up to 10 mM) is significantly higher than that in normal tissues. Based on the above, the core-and-shell structure nano drug delivery system with mitochondrial targeting was designed. The core is a cationic polypeptide-based block copolymer with side chains containing esters of benzene- boronic acid, which can load photosensitizer chlorin e6 (Ce6) and autophagy inhibitor through non-covalent interactions. The negatively charged outer shell is PEG-b-polylysine-graft-cis-aconite anhydride, which disintegrates in the acidic environment. The effective endosomal/lysosomal escape of nanoparticles may be as a result of the proton sponge effect of polycationic polymers and autophagy inhibition. The inner-layer particle located in mitochondria can oxidize boronic esters and consume GSH, which increases the accumulation of the ROS caused by C6-mediated PDT. Blocking autophagy aggravates the toxicity of excessive ROS, which synergistically triggers tumor apoptosis or necrosis. In this work, the double drug-contained system is designed in the treatment of glioblastoma, in order to investigate the effect of combined autophagy inhibition and GSH consumption on the oxidative stress. The synergistic anti-tumor strategy exploits a novel way for the development of ROS-based combination therapy.

Keywords

nanoassemblies, glioblastoma, oxidative stress, autophagy

P2.18

Stability of MWCNTs functionalized with surface oxygen groups: wet chemistry vs. plasma treatment

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Abstract

Since raw carbon nanotubes (MWCNTs) are entirely hydrophobic, their applications as biomaterials require surface functionalization. Such modifications are one of the main strategies to improve the dispersibility in the polar solvent of choice. Additionally, the presence of functional groups enables the anchoring of molecules to carbon surfaces, including attachment of bioactive compounds. For carbon-based biomaterials, oxygen-containing functional groups (-COOH, -OH, -CHO) are most often introduced. Polar oxygen groups due to the electronegativity difference between carbon and oxygen atoms affect mostly the wettability of the carbon surface and its electron-donor properties. These parameters are considered key in biocompatibility as the work function was indicated as a suitable parameter to assess the quality of biomaterials' surface.

The work aimed to investigate the effect of the functionalization of multi-wall carbon nanotubes using the wet chemistry method and oxygen plasma treatment on the surface properties of the carbon materials. The materials were functionalized with the use of wet chemical methods ($\text{H}_2\text{O}_2+\text{H}_2\text{SO}_4$; $\text{H}_2\text{SO}_4+\text{HNO}_3$) or oxygen plasma. Raman spectroscopy revealed significant differences in the intensity ratio of the ID/IG maxima for the samples obtained with wet chemical methods (increase in the ID/IG ratio). The changes in electrodonor properties (changes in work function values) of MWCNTs were measured using Kelvin Probe. Both of the modifications used in the study increased the work function values, i.e. for wet chemical methods, $\Delta\Phi = 0.1-0.3$ eV, while for the plasma treatment $\Delta\Phi = 0.7-1.1$ eV. The effect of functionalization was evaluated in terms of the quality of the obtained suspensions in polar solvents by monitoring the sedimentation of MWCNTs over 36 days. It was observed that wet chemical functionalization is stable for more than 30 days, while plasma treatment diminishes within 24h.

This study was supported by the National Science Centre, Poland, under grants no. UMO-2017/24/C/ST8/00400 and 2020/37/B/ST5/03451.

Keywords

carbon nanotubes, functional groups, Surface functionalization, Work function

P2.19

Co@Cu-CeO₂ core-shell catalyst designed by hydrothermal synthesis with enhanced high-temperature durability and low temperature activity for CO and C₃H₆ simultaneous oxidation

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Abstract

When fuel is burned in an internal combustion automobile engine, various harmful substances are emitted as exhaust gas, among them carbon monoxide (CO), hydrocarbon (HC), particular matter (PM) and nitrogen oxides (NO_x). Regulations on these substances, such as Euro 7 and LEV3 are getting tighter around the world. However, since it is difficult to simultaneously satisfy high fuel efficiency and low emissions with the existing internal combustion engine purification system, it is necessary to develop a new catalyst that starts to show activity at a low temperature of 150 °C or less to achieve high fuel efficiency and low emissions. Moreover, since the temperature of an automobile engine can reach up to 1000 °C depending on driving conditions, the catalyst is also required to be durable at high temperatures.

Platinum group metal (PGM) catalysts, which are widely used in internal combustion engine engines, have excellent CO activity, but when HC is present, the activity is lowered due to the competitive adsorption of these two gases. However, the CCC catalyst composed of Co, Cu, and CeO₂ has excellent activity because the active sites of the two gases are separated.

So, in this study, the catalyst composed of Co@Cu-CeO₂ was introduced. However, it is reported that cobalt catalyst is vulnerable to sintering of the catalyst at high temperature. To prevent this, cobalt was synthesized in cubic shape and a core-shell structure was introduced. Co₃O₄ cubes were prepared by hydrothermal synthesis first as the core, and this was followed by a controlled CeO₂ shell coating process and Cu was introduced by incipient wetness method. By controlling the thickness of the shell, optimal CO and C₃H₆ activity was sought and durability evaluation after hydrothermal aging at 750 °C and characterization analysis were performed.

Keywords

Hydrothermal synthesis, CO and C₃H₆ co-oxidation, Co@Cu-CeO₂ catalyst

P2.20

Advances in top down approaches for borophene fabrication

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Abstract

Two dimensional (2D) materials are catching enormous interest in recent years due to their unique properties, e.g. electrical conductivity, intriguing active surface. The development of advanced carbon materials i.e. graphene and its derivatives put other 2D materials into the spotlight, therefore new 2D materials are widely explored. Notwithstanding well-known graphene, transition metal dichalcogenide (TMD) like WS₂, MoS₂, MoSe, and WSe have been intensively studied. Moreover, hexagonal boron nitride (hBN), black phosphorus and recently, successfully manufactured borophene are subject of research. Borophene presents intriguing properties due to its anisotropy, polymorphism and crystal structure. Despite the bulk boron occurs a B₁₂ icosahedron as a basic structural unit, the various types of boron crystals being formed through different connections and bonding methods on the B₁₂. Therefore, the boron block is not typically layered like graphene or graphite, which leads to more advanced techniques of borophene synthesis. In addition, many polymorphism forms e.g. α , β , $\alpha 1$, pmmm make it even more complicated. Numerous synthesis methods of 2D materials are based on sonochemical processes, where bulk material is put in a solvent and is subjected to ultrasounds for many hours. Despite that, atomic layer deposition (ALD) is one of the bottom-up methods to synthesis borophene, where boron atoms are deposited onto atomically clean silver support. One of the noncomplicated exfoliation of boron methods is the utilization of simple adhesive tape.

Here, we present advances in the top down approaches to fabricate few-layered borophene. Presented results will be supported by detailed high resolution microscopic investigation and fundamental physico-chemical characterization. It is believed some of the approached can be scale up towards fabrication of borophene in a scale allowing detailed exploration of this new family member of 2D materials.

Keywords

borophene, 2D materials, fabrication, characterization

P2.21

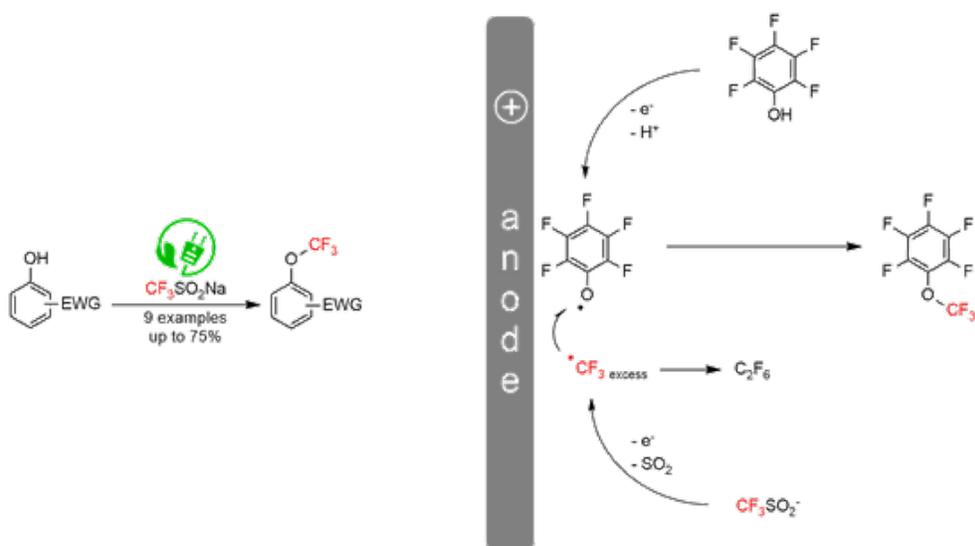
Electrochemical *O*-trifluoromethylation of electron-deficient phenols

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Abstract

A simple and sustainable one-step strategy for the preparation of electron-deficient aryl trifluoromethyl ethers (ArOCF₃) from the corresponding phenols by electrochemical synthesis is presented. Anodic oxidation of trifluoromethane sulfinat (Langlois reagent) leads to direct *O*-trifluoromethylation of phenol-derivatives bearing fluorine, chlorine, bromine and nitrile substituents under mild conditions in yields up to 75% and in gram-scale. This electrochemical protocol provides an economic and green synthesis for an otherwise inaccessible class of molecules without the need for expensive or toxic reagents, oxidants or metal catalysts.^[1]



Literature:

[1] J. Bernd, P. Werner, M. Zeplichal, A. Terfort, Electrochemical *O*-trifluoromethylation of electron-deficient phenols, *Electrochem. Commun.* **2021**, 133, 107165.

Keywords

Organic electrochemistry, Anodic oxidation, Trifluoromethylation, Green chemistry

P2.22

A modelling study of interfacial polyamidation

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Abstract

Interfacial polymerization (IP) is a popular fast polymerization technique that doesn't need severe operating conditions like other polymerization techniques. Its main applications are in thin-film composite membranes and microencapsulation, but it can also be used for the production of bulk polymers that are thermo-labile and cannot be produced by other methods. The fast reaction kinetics, and complex array of several transports, reaction, and equilibrium processes, make its mathematical modelling challenging. Thus, very few attempts have been made to model IP reaction, especially to predict the film properties such as film thickness, molecular weight distribution, crystallinity, and polydispersity. The work of Dhumal and Suresh (2009) on polyurea system does address both kinetics and film properties but is not applicable to the commercially important polyamide system, in which the liberation of HCl brings in some unique complications and features.

This work extends the work of Dhumal and Suresh (2009) to the interfacial reaction of a diamine with a diacid chloride. Our model accounts for different physicochemical processes associated with the reaction, such as ionic equilibria in the aqueous phase, external mass transfer, monomer diffusion through the film, solution thermodynamics, phase separation kinetics, and film formation. Flory-Huggins theory has been used for solution thermodynamics. A competition between nucleation and spinodal decomposition-based phase separation has been postulated to predict the film's crystallinity.

From earlier studies, it was evident that only the unprotonated amine takes part in the reaction, which underlines the importance of pH. For the case of polyamide formation via the IP route, HCl is a byproduct of the reaction and restricts monomer availability in the reaction zone. The present model explains the experimental observation that the reaction ceases despite both monomers being still available due to the amine monomer being almost entirely protonated by about 33% conversion.

Keywords

Interfacial polycondensation, Flory Huggins theory, ionic equilibrium, reaction kinetics

P2.23

Ultra-short laser processing of 3D bioceramic, porous scaffolds designed by Freeze Foaming method for orthopaedic applications

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Abstract

Bone substitutes are widely employed for applications in orthopaedic surgery for replacement of injured bone. Among the diverse methods that are used to design a 3D bioceramic matrices, Freeze Foaming has gained attention, since it provides the ability to tune the shape of the created structures. One of the major problems related to these constructs are the lack of porosity at the outwards sides (holder) of the scaffold, thus reducing the cellular affinity and creating a rejection of the implant. In this research our aim was to develop a bone scaffold with enhanced surface property and improved cellular affinity. The main aim was to alter the biocompatibility characteristics of the 3D bioceramic constructs. We have produced a three dimensional, complex-shaped hollow shell structures, manufactured by Additive Manufacturing processes and as a second step, filled with a ceramic suspension by Freeze-Foaming process. A 3D constructs from CaP/ ZrO₂ were synthesized by freeze-foaming method and subsequently irradiated with a fs-laser ($\lambda=800$ nm) spanning a range of parameters for achievement of optimal surface processing conditions. The designed scaffolds demonstrated an enhanced topographical properties with improved porosity examined by SEM and EDX after laser treatment. The results from X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and computer tomography (CT) analysis didn't show photochemical and surface or volume defects, changes after laser processing of the ceramic samples. Preliminary results from MG-63 osteo-blast-like cell tests showed good cell affinity on the processed surfaces.

Acknowledgments: This work was supported by EUROPEAN UNION'S H2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement AIMed No. 861138; BULGARIAN NATIONAL SCIENCE FUND (NSF) under grant number No. KP-06-H48/56(2020-2023), and H2020 FET Open METAFast Grant Agreement No. 899673.

Keywords

Ultra-short laser processing, biomaterials, tissue engineering, surface functionalization

P2.24

Solid state dispersions of platinum in the SnO_2 nanomaterials

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Abstract

Cassiterite (SnO_2) nanoparticles were synthesized by activating Sn(II) acetate in a planetary mill followed by heat treatment at 600 °C. FTIR results showed that milling of the acetate precursors in a planetary mill did not result in the degradation of acetate groups (FTIR bands at ~ 1517 and $\sim 1391 \text{ cm}^{-1}$). The volume-averaged domain size of the cassiterite was estimated to be ~ 29 nm. The results of Williamson-Hall analysis of the cassiterite sample indicated the presence of anisotropy, with slightly larger crystallite size in the direction parallel to the broadening axis $hk2$ (estimated at ~ 34 nm). Platinum (Pt) in the samples was detected directly by EDXS analysis and indirectly by TPR results (Temperature Programmed Reduction in hydrogen, H_2). SnO_2 was reduced with H_2 , according to the simplified equation $\text{SnO}_2 + 2 \text{H}_2 \rightarrow \text{Sn} + 2 \text{H}_2\text{O}$. The H_2 -TPR curve of the pristine SnO_2 sample showed that the reduction of SnO_2 started at about 180 °C and ended with an "incomplete" maximum at 643 °C. The incomplete reduction of SnO_2 to Sn can be attributed to the formation of the Sn metal shell around the SnO_2 particles. The melting point of tin is very low at 232 °C, so molten tin on the surface of SnO_2 particles can protect Sn^{4+} from reduction. The addition of Pt promotes the reduction of SnO_2 , and the reduction started at a lower temperature (~ 100 °C) and ended with a well-defined maximum at 652 or 733 °C. XPS results confirm the presence of Pt^0 and Sn^0 , whereas the XRD results assigned Pt, PtSn, Pt_2Sn_3 , PtSn_2 , PtSn_4 . The catalytic properties of synthesized Pt/ SnO_2 nanomaterial were investigated.

ACKNOWLEDGEMENTS: This work was financially supported by Croatian Science Foundation under the project UIP-2019-04-1195 "Platinum decorated iron tin oxide solid solutions for hydrogen gas sensing" (HydGasSens).

Keywords

platinum, cassiterite, dispersion, ball-milling

P2.25

Tailoring surface chemistry of cytocompatible CNTs for enhanced anticancer and antibacterial properties

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Abstract

Carbon nanotubes (CNTs) are promising nano-based tools for infection control and anticancer therapies. CNTs can enable the photothermal and photodynamic therapies (PTT and PDT), combine multiple binding mechanisms (π - π stacking, covalent and non-covalent chemical bonding to the CNT's walls, and loading inside the cavity), and enter the cells through different intake mechanisms (passive diffusion or dynamin-dependent pathways).

All of the above-mentioned qualities are governed mainly by the CNTs' chemical structure and surface properties. These, in turn, strongly affect the materials' cytocompatibility. Hence, designing the CNTs to be used in the anticancer/antibacterial applications should always include careful designing of the specific types of surface modifications.

In this study, 5 types of CNTs, differing in their chemical composition were prepared and characterized in terms of their physicochemical properties (type and amount of surface functional groups, sizes and structures, electro-donor properties) and biological performance (cytocompatibility, anticancer and antibacterial effects). Unmodified CNTs (uCNTs), two types of oxidized CNTs differing in the oxidation states (mainly +2 (LOp) or +3 (HOp)), amine (LNHp) and amide (HNHp) functionalized CNTs were chosen for the study in order to provide a broad spectrum of chemical states the CNTs can exist in.

LOp and LNHp and uCNTs were characterized by a high tendency to form agglomerates and a low cytocompatibility. Meanwhile, the HOp and HNHp were characterized by good dispersibilities, high ROS production efficiency, both in macrophages and HDF cells, while their cytocompatibility was satisfactory. At the same time, strong antibacterial and sensible anticancer effects were observed.

It can be concluded that careful tailoring of the CNTs' surface chemistry allows for obtaining cytocompatible and effective cancer and bacteria targeting nanomaterials.

Keywords

Carbon nanotubes, work function, antibacterial, surface chemistry

P2.26

Synthesis of magnetic iron oxide/Au and iron oxide/Ag nanostructures using a simple γ -irradiation method

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Abstract

In this work we have used γ -irradiation as an efficient and environmentally friendly technique for the synthesis of magnetic nanoparticles. γ -irradiation has the advantage of inducing electrons and other reducing species uniformly in the sample. The alkaline aqueous iron(III)chloride solutions were purged with nitrogen and γ -irradiated with addition of 2-propanol. DEAE-dextran was used as a growth and stabilizing agent for MNPs in suspensions. The phase composition, stoichiometry, and morphology of MNPs were controlled by adjusting the γ -irradiation dose. Irradiation with doses 10-36 kGy resulted in the formation of 4 nm spherical sub-stoichiometric magnetite NPs, while at higher doses (50 kGy or more) the main phase was magnetic δ -FeOOH (feroxyhyte) in the form of nanodiscs. Magnetic measurements revealed superparamagnetic behavior of magnetite NPs and exceptional intrinsic magnetic properties of δ -FeOOH nanostructures at room temperature with a Curie temperature above 300 K. Reduction of Fe^{3+} to Fe^{2+} was quantitatively determined using 1,10-phenanthroline spectrophotometric method. The reduction is rapid in the initial stages of irradiation ($\sim 65\%$ of Fe^{3+} is reduced up to 30 kGy), then slows down and reaches 100% at ~ 75 kGy. The reduction power of Fe^{2+} in irradiated suspensions was explored to synthesize iron oxide/Au nanostructures by adding aqueous HAuCl_4 solutions to the irradiated suspensions. Microstructural and morphological analysis showed that the simultaneous oxidation of $\text{Fe}(\text{OH})_2$ and reduction of Au^{3+} led to the formation of δ -FeOOH nanodiscs decorated with small spherical AuNPs. The density and size of AuNPs on the surface of nanodiscs depended on the concentration of added aqueous HAuCl_4 solution. The same procedure was used for the synthesis of δ -FeOOH nanodiscs with AgNPs on the surface. The synthesized magnetic nanoparticles were tested for their SERS and catalytic activity.

Acknowledgments: This work has been supported by the Croatian Science Foundation under the project UIP-2017-05-7337 (POLRADNANOP).

Keywords

feroxyhyte/Au, feroxyhyte/Au, γ -irradiation , iron-oxide nanoparticles

P2.27

Role of pulse amplitude and pore-widening in the fabrication of gradient-index infrared filters based on porous anodic alumina

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Abstract

Due to the acceleration of sustainable development in human society, a better understanding of the light-matter interaction becomes increasingly important for constant improvements in the engineering of interferometers, cameras, thermal energy storage and optical chemosensing devices. The photonic crystals made of porous anodic alumina are very desirable for controlling infrared light and open new perspectives in thermal photonics. Transparent heat mirrors must be highly absorbing over the solar spectral region and reflect thermal radiation with longer wavelengths ($> 2.5 \mu\text{m}$). Such a mirror should demonstrate broadband and a spectrally-selective reflection of the thermal radiation. Optical sensor, on the contrary, requires sensitivity and chemical selectivity toward chemical species thanks to a narrow and tunable photonic stop-band. Anodization enables simple and affordable production of porous photonic crystals with such different optical properties by designing appropriate pulse sequences and suitable electrochemical conditions. We will demonstrate how the parameters of the sinusoidal pulse anodization at high temperature (30 °C) enable the change of photonic stop-band behaviour, such as the red-shift of the photonic stop-band and a change of reflectance value. We varied the pulse amplitude magnitude for controlling the intensity of higher-order reflection, enabling the production of porous anodic alumina-based optical platforms for different application purposes. Furthermore, the pore-widening process appears as a suitable post-synthesis crystal modification to the blue-shift of the photonic stop-band and the simultaneous increase of the reflection intensity.

During the talk, we will present how the amplitude of sinusoidal pulse and pore-widening affect the optical properties and microstructure of porous anodic alumina platforms. Moreover, we will show that the porous anodic alumina platform is particularly well suited to the reflection of the infrared wavelength region with the possibility of further enhancement. The technical aspects related to the optical characterization of porous anodic alumina platforms will be raised as well.

Keywords

photonic crystal, pulse anodization, optical sensor, photonic stop-band

P2.28

Stability of Novel Eco-friendly Sulfated Metal Oxide Solid Acid Catalyst for Esterification and Condensation Reaction

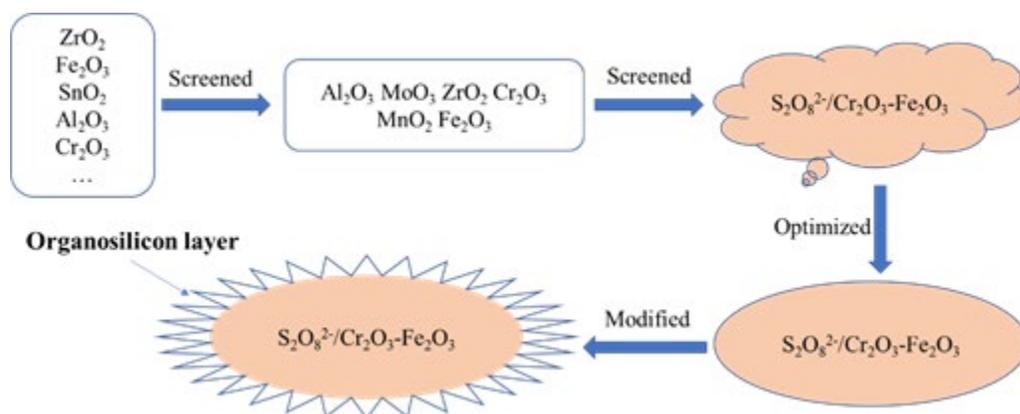
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Abstract

The metal oxide supports and active component precursors of $\text{SO}_4^{2-}/\text{MxO}_y$ solid acid for esterification reaction were screened, and $\text{S}_2\text{O}_8^{2-}/\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ($\text{S}_2\text{-CrFe}$) was prepared. The $\text{NH}_3\text{-TPD}$ results showed that the solid acids loaded with $\text{S}_2\text{O}_8^{2-}$ had stronger acidity than those loaded with SO_4^{2-} , and the mixture of the two metal oxides could adjust the acidity of the solid acids. The optimum conditions for the preparation of $\text{S}_2\text{-CrFe}$ were as follows: the mass ratio of Cr_2O_3 to Fe_2O_3 was 1, the concentration of ammonium persulfate solution was 1 mol/L, and the calcination temperature was 550 °C. The yield of esterification catalyzed by the solid acid obtained under these conditions was 91.2%. It was found that $\text{S}_2\text{-CrFe}$ was seriously deactivated after being recycled for four times in the esterification reaction, i.e., after four cycles, the yield of ethyl acetate under modified catalyst was over 50% while that was below 50% under unmodified catalyst. So it was considered to modify the surface of new solid acid with organosilane. The experimental results showed that organosilane could effectively improve the stability of solid acid. Finally, the new solid acid was applied to the condensation reaction of ethylene glycol and butanone. Due to the timely separation of water in the process, the modified solid acid showed excellent stability and almost no deactivation after recycling.



Keywords

Metal oxide, Solid acid, Stability, Surface modification

P2.29

Lithium-decorated Popgraphene, an analysis of stability and capacity for hydrogen storage

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Abstract

The successful realization of extended '5-5-8' line defects in graphene in a controlled way has suggested the possible formation of a new 2D carbon allotrope consisting in pentagonal-octagonal-pentagonal carbon rings. The mechanical and thermal stability of this nanostructure, called popgraphene, has recently been confirmed on the basis of first principles calculations. Moreover, it has been proposed as a promising anode material for use in Li-ion batteries with fast charge/discharge rates.

We investigated at density functional theory level the hydrogen storage ability of popgraphene. After a detailed search for stable configurations, we found that the suitable Li-decorated popgraphene sheet can bind up to four H₂ molecules per unit cell, with an average adsorption energy in a range between physisorption and atomic chemisorption, which would allow for reversible hydrogen storage at moderate temperatures and pressures. Moreover, the gravimetric density of the Li-decorated popgraphene is 4.24 wt%, which is almost equal to the threshold specified by the U.S. Department of Energy for novel hydrogen-storage materials. All these results show that Li-decorated popgraphene nanostructures could be good materials for hydrogen storage.

Keywords

Popgraphene, H₂-adsorption, Van der Waals-corrected DFT, Hydrogen storage

P2.30

Improvement of surface conditions of silk thin films via ultra-short laser texturing for creation of muscle cell matrix model

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Abstract

Severe burns, lacerations, or various muscle injuries often require tissue transplantation from either the patient himself or from a donor. Traditional treatment options have many negative consequences for the recipient, such as a new injury creation, additional infections and a high immune response. Tissue engineering on the other hand relies on temporary cellular scaffolds that mimic the extracellular matrix and provide a stable structure for the natural growth of muscle cells. Silk fibroin (SF) is one of the most preferred natural polymers for this purpose due to its unique mechanical properties, elasticity, controlled biodegradability rate and high biocompatibility. Our aim is to obtain and design porous 2D fibroin-based cell matrices by femtosecond laser-induced microstructuring for future application in muscle tissue engineering. Ultra-fast laser treatment is a non-contact method, generating strictly controlled porosity - the creation of micro/nanostructures on the surface of the biopolymer can strongly affect cell behavior, while the control over its surface characteristics has the potential of directing the growth of future muscle tissue in the desired direction. The laser structured 2D matrices were characterized by means of SEM, EDX, FTIR and roughness analyses. Initial cellular experiments were also performed. The results show that by varying the laser parameters different structuring degree can be achieved - from initial lifting and ejection of material around the area of laser interaction to generation of porous channels with varying width and depth. Proper optimization of laser parameters applied can significantly improve the bioactive properties of the investigated 2D model of muscle cell matrix.

Acknowledgments: The authors acknowledge the support from Bulgarian national science fund (NSF) under grant number No. KP-06-Austria / 5 (2021-2023) and EUROPEAN UNION'S H2020 research and innovation program under the Marie Skłodowska-Curie Grant Agreement AIMed No. 861138.

P2.31

A new functional antibacterial coating for preventing peri-implantitis disease in dental implants

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Abstract

In this work, a novel multifunctional coating has been developed to prevent peri-implantitis disease associated with dental implant infection. This coating fulfilled the demanded requirements of specificity, temporal stability, durability, tribocorrosion resistance and minimum toxicity. For this purpose, TaNCu_x thin film coatings with different copper concentrations (x) were deposited by magnetron sputtering on medical grade Ti-implants to enhance its multifunctional performance. Tantalum (Ta) has been considered a promising biomaterial for dental implants, orthopaedic and arthroplasty applications due to its preferred biocompatibility and osteogenic properties. The combination of TaN and Cu was selected to tune their performance in terms of mechanical, tribological and antibacterial performance for specific bacteria (both gram-negative and gram-positive) linked to peri-implantitis (*Rothia dentocariosa*, *Treponema denticola* and *Staphylococcus aureus*). The new surface achieves antimicrobial properties with 99.999% (log 5) bacteria reduction and the toxicity requirements for dental implant. In a nutshell, the multifunctional coating developed shows a promising solution for fighting against peri-implantitis, a disease affecting 20% of patients and 30% of implants. Additionally, the surface engineering technology described in this work can be industrially implemented as a common post-processing high throughput manufacturing technology for dental implants.

Keywords

Antimicrobial, Dental implant, Coating, Magnetron Sputtering

P2.33

Quantification of nitrogen in the high temperature oxidation of titanium in air

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Abstract

Titanium alloys are widely used in the aerospace industry, for example in turbojet engines, thanks to their good mechanical properties and corrosion resistance. Specific mechanical surface treatments, like laser shock peening, could extend their application to higher temperature. Such treatments already highlighted the role of nitrogen in the high temperature oxidation. By accumulating at the oxide/metal interface, nitrogen tends to slow oxidation, decrease the stratification of the oxide layer and increase the adhesion of the oxide layer to the metal.

Nevertheless, many questions remain unanswered, like: how much nitrogen is involved in the process as a function of time? This article answers this question with analysis realised on a series of commercially pure titanium samples oxidized in air at 650°C from 15 min to 100 h. The characterizations focused on the behaviour of nitrogen in terms of kinetics, location and chemical interactions. After oxidation, analysis by X-ray diffraction, scanning electron microscopy, glow-discharge optical emission spectrometry (GDOES), secondary ion mass spectrometry (SIMS), and ion beam analysis (IBA) were carried out.

It is shown that nitrogen appears to insert into titanium from the early stages of oxidation, accumulating at the oxide/metal interface to form Ti_2N and a possible oxinitride. As the oxidation time increases, nitrogen seems to spread out in the oxide (oxinitride) and in the metal (Ti-N). GDOES analysis suggests a parabolic kinetics of the nitrogen insertion during the oxidation in air, which was, at our knowledge, never noticed before. Since the overall mass gain measured by thermogravimetric analysis is also parabolic, we can assume that nitrogen limits oxidation.

The IBA analysis allows deducing the quantity of nitrogen part of the overall mass gain. A comparison with mass gain curve obtained under $Ar+O_2$ atmosphere permits to quantify the influence of the nitrogen on the oxidation in air.

Keywords

High temperature oxidation, Titanium, Nitrogen, Ion Beam Analysis

P2.34

Manufacturing Smart Surfaces with Embedded Sensors via Physical Vapour Deposition and Laser Scribing

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Abstract

Smart surfaces are material surfaces that integrate functional systems that add active monitoring and/or actuation capabilities. This study presents a novel method to manufacture smart surfaces with integrated sensors and actuators via Physical Vapour Deposition (PVD) and Laser Scribing (LS). For that, the target surface is coated by PVD with a 2-3 μm insulator layer (usually a metal oxide such as SiO_2 , Si_3N_4 or Al_2O_3), and afterwards with a 0.5-2 μm metallic conductor layer. Alternatively, a 15 μm dielectric lacquer deposited by spray coating is used as the insulator layer. The conductor is then selectively removed by LS without removing the insulator to draw a circuit completely isolated from the piece. The scribing of the circuits is done with a femtosecond laser ($\lambda=517\text{ nm}$) that allows extremely quick ($\sim 200\text{ mm/s}$) and accurate manufacturing of a sensor in a few seconds with $\sim 30\text{ }\mu\text{m}$ space resolution. The type of sensor is determined by the selection of the conductor(s) and insulator(s) materials and the shape of the circuit, and can be manufactured to match the specifications of the application by modifying the PVD and LS parameters. In this work two types of embedded sensors were manufactured and tested: resistive temperature detectors made of Al, Ti, W or Cu, and strain gauges made of NiCr. These embedded sensors can measure with a high degree of precision as they are directly connected with the piece without adhesives or polymer foils, and even without humidity, organics, or oxygen in between. In addition, this technology allows to locate sensors in components with complex geometries, in places difficult to access with a traditional sensor, and as the sputtered sensors are only a few micrometres-thick they do not affect the dimensional tolerance of the piece.

Keywords

Smart Surfaces, Physical Vapour Deposition, Laser Scribing, Sensor

P2.35

Poly(hydroxybutyrate-co-hydroxyvalerate) as a biodegradable binder in a negative electrode material for lithium-ion batteries

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Abstract

A biodegradable binder, poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), belonging to polyhydroxyalkanoates family is presented as an alternative material able to replace polyvinylidene fluoride (pVDF) in battery application. Plastic binders are known to undergo degradation during battery utilization and it may lead to release microplastics that affect the environment [1]. Thus, it is still a need to find an eco-friendly binder of natural origin able to be biodegradable.

The studied PHBV material is thermoplastic, from renewable sources, biodegradable, compostable and biocompatible polymer that is utilized in biomedical [2] and pharmaceutical applications [3].

In this work, we report our investigation on the use of environmentally friendly, biodegradable and low-cost binder PHBV as an alternative material for composite negative electrode with commercial graphite as an active material. For comparison PVDF was used as a reference binder. The scanning electron microscopy (SEM) was utilized to get a better view on the solid electrolyte formation (SEI) process of cycled and non-cycled electrode materials. Electrochemical measurements such as electrochemical impedance spectroscopy (EIS) and galvanostatic intermation technique (GITT) were performed to calculate lithium-ion diffusion coefficient. Moreover, the influence of the electrode potential on the transport of lithium ions was studied. Galvanostatic tests exhibited that PHBV based electrode was stable during charging/discharging.

The result showed in this paper clearly demonstrates the feasibility of using green-materials and green processing to produce Li-ion batteries.

Acknowledgment

Financial support from The National Centre for Research and Development (grant no LIDER/15/0088/L-10/18/NCBR/2019) is gratefully acknowledged.

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Keywords

lithium-ion battery, anode material, biodegradable polymers

P2.36

Corrosion products on aluminium surfaces: gentle removal with phosphonylated polyethylenimines

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Abstract

Nowadays, a responsible approach for use and handling of limited resources is more important than ever. Especially the efficient use of energy resources is in the economic and environmental focus. Aluminium, often used for parts in heat operating machines like heat exchangers, suffer from formation of surface-bound corrosion products which lead to poorer heat transfer and a reduction of efficiency level. For removal, harsh conditions like mechanical excision and etching are used, resulting in further damage to the surface. Therefore, a method is needed that works under mild conditions. Here we present an analytical study in which we investigated the gentle removal of corrosion products from technical aluminium surfaces using phosphonylated polyethylenimines. For basic investigations, a model system was designed based on defined aluminium sheets that were exposed to sulphurous acid for formation of surface-bound corrosion products. Phosphonylated polyethylenimines were obtained by the reaction of polyethylenimine with formaldehyde and phosphonic acid in a Moedritzer-Irani reaction. Removal of the surface-bound corrosion products was tested through incubation of the corroded sheets in the synthesized phosphonylated polyethylenimines under various conditions (pH, polymer concentration). Evaluation of the experiments was carried out with digital optical microscopy and surface scanning electron microscopy. After determining the most efficient conditions for removal of the corrosion products, the experiments were repeated on corroded surfaces of a dismantled heat exchanger and evaluated for their effectiveness on technical aluminium surfaces.

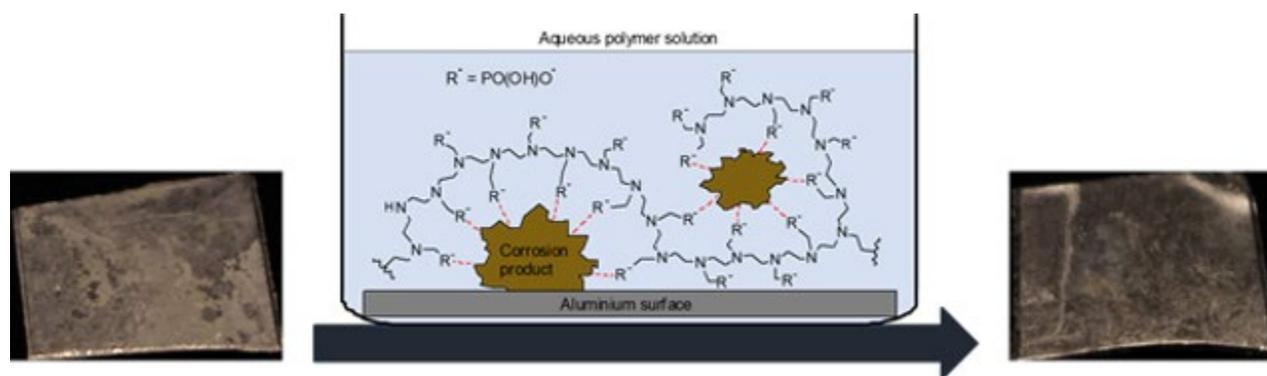


Fig. 1: Model system based on aluminium sheets (ca. 1cm x 1cm) with surface-bound corrosion products. After incubation in an aqueous solution of phosphonylated polyethylenimine ($R' = PO(OH)O^-$), the corrosion products were removed, and a clean aluminium surface was obtained. By using the phosphonylated polymers, etching and further damage to the surface could be avoided.

Keywords

Surface corrosion, Polyethylenimine, Aluminium

P2.37

Electrowetting properties of [BMIM][BF₄] humid ionic liquid in graphene channel

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Abstract

Ionic liquids as electrolytes for supercapacitors are attracting lots of attentions because of its good thermal and chemical stability at room temperature, extremely low osmotic pressure, designability and other advantages. The existence of water in the ionic liquid might affect the double electric layer in the solid-liquid interface and then affect the capacitance of in the supercapacitors. In this paper, molecular dynamic simulation was adopted to investigate the wetting and electrowetting phenomenon of [BMIM][BF₄] ionic liquid mixed with water in the channel of graphene. And the effect of temperature is also discussed. The result shows that water molecules adsorb near the solid graphene surface and this adsorption phenomenon becomes obvious with the increase of the amount of water in the ionic liquid, resulting in an increase in the contact angle of ionic liquid on the graphene surface. Ionic liquid and water molecules rearrange themselves under the effect of electric field and tend to spread on the solid surface, and the contact angle of ionic liquid on the graphene surface decreases with the increase of electric field. The results provide a theoretical basis for the application of ionic liquids in supercapacitors.

Keywords

Electro-wetting, Interface phenomenon, Ionic liquids, Molecular simulation

P2.38

Hydrate crystal growth on water droplets: roles of wettability based on modified substrates

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Abstract

The gas hydrates bring serious and common engineering disasters in flow assurance, and modified surfaces with various wettabilities have been developed to mitigate the impact of hydrate plugs in pipelines recently. However, studies on the hydrate growth characteristics on water droplets in contact with surfaces of different wettabilities are limited. Therefore, in this study, the effects of hydrophilic, untreated, hydrophobic and superhydrophobic surfaces on hydrate growth and hydrate crystal morphology were investigated. The microscopy results showed that there are two types of characteristic behaviors: along-surface growth and off-surface growth on surfaces with varying wettability. On hydrophilic surfaces, the hydrate grew outside the original water boundary, known as the halo effect, which was observed on the prepared hydrophilic surface. On the untreated surface, the halo effect also occurred, though the hydrate layer was thicker and rougher. Importantly, the halo effect was not observed on the hydrophobic surfaces. The hydrate layer was first smooth and then depressed. The experimental results illustrate that subcooling is a factor that influences the morphology of the xenon hydrate crystal. Furthermore, the hydrate propagation rate and growth rate along the surface of the water droplet were also observed. The hydrate propagation rate on the hydrophilic surface is greater than that on the untreated surface. The hydrate growth rate on the hydrophobic surfaces is extremely high, and the growth of the hydrate layer in the field-of-view was usually completed within 1-3 s. This study provides insights into the growth characteristics of hydrates on varying wettability surfaces, and the results suggest that hydrophobic surfaces could mitigate the adverse effects of hydrate deposition and blockage in the pipeline.

Keywords

hydrate plug, crystal growth, modified surfaces, wettability

P2.39

2D/0D SnS multi-structure for assist high performance hydrogen evolution photocatalyst

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Abstract

The study of layered two-dimensional (2D) materials is at the forefront of materials science. Among them, Black phosphorus, a representative next-generation star, has very attractive characteristics, but there is a stability issue that it is weak to water and air exposure. To overcome this, a black phosphorus analogue material that has similar advantages to black phosphorus and has secured stability can be substituted. A 0D/2D composite tin monosulfide (SnS) photocatalyst was designed and synthesized by controlling the shape of this material whose band gap is controlled according to its thickness. The photocatalytic activity of this complex was significantly improved compared to the single material with the reaction rate constant k . In addition, this material helped the CdS material to show a dramatic hydrogen evolution efficiency. This mechanism was analyzed by the Time-resolved Photoluminescence method. Tin monosulfide different dimension shape has a different band gap, so it can act as a donor / acceptor like the heterojunction. This increases the lifetime and reduces the recombination rate. Designing and fabricating bandgap energy-matched nanocomposite photocatalysts may provide a fundamental direction to solve future clean energy challenges.

Keywords

2D materials, Quantum dots, Photocatalyst, Hydrogen evolution

P2.40

The effect of Bias configuration on the properties of AlCrN based thick coatings deposited by Cathodic Arc Evaporation

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Abstract

Die wear in forming high strength steels (HSS) operations causes increased die maintenance cost and scrap rate, being a major obstacle for automation industries to meet upcoming market requirements. Continuously increasing strength of HSS sheets requires a new surface solution on tooling; current surface treatment solutions (CVD coatings or a combination of plasma nitriding plus 5 μm PVD coating) involve time consuming and expensive processes and show low tolerances and performance of dies when working with HSS.

Advanced PVD coatings of high thicknesses can be optimum solution from both an economic and technical point of view. Cathodic Arc Evaporation is the mostly widespread deposition technology for the production of industrial hard coatings due to its high energy and high deposition rate. However, growing thick PVD coatings (20 μm) at productive speeds requires a thorough process optimization in order to minimize residual stresses in the coating during its growth while ensuring optimal mechanical properties of the coating. Bias voltage is a key parameter to obtain this goal.

In the present study, an innovative approach combining an advanced substrate pre-treatment and a new generation of ultrathick hard AlCrSiN coatings grown at high deposition rates was developed by cathodic arc evaporation. Different Bias configurations have been applied for the deposition of these AlCrN based coatings; a conventional DC continuous and a Bipolar signal modulated under different frequencies. The effect of these different Bias options on the basic and mechanical properties of the coatings has been analyzed. For that purpose, coating characterization by means of deposition rate, adhesion, microstructure, composition, structural phases, residual stresses and hardness has been carried out by using scanning electron microscopy (SEM), Rockwell and Scratch test, GDOES, X-ray diffraction and nanoindentation.

The results show the clear influence of Bias modulation in the coating properties and performance.

Keywords

PVD, Bipolar Bias, AlCrN based, Residual stress

P2.41

TiO₂ nanotubes modified by Ti-Fe₂O₃/In₂O₃ for highly efficient photoelectrochemical water oxidation

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Abstract

Since the photocatalytic decomposition of water using crystalline TiO₂ was first described by Fujishina and Honda [1], a number of different semiconducting metal oxides have been studied, such as ZnO, WO₃ and Fe₂O₃ have been studied [2,3]. The main steps in photocatalytic reactions are: (1) photoexcitation of charge carriers; (2) separation of charge carriers and diffusion to the photocatalyst surface; and (3) oxidation and reduction reaction on the catalyst surface. During step (2), recombination of charge carriers can occur which must be inhibited to improve the performance of the photocatalytic reaction [4]. Several approaches have been reported in the literature to inhibit charge carrier recombination in heterogeneous photocatalysis, such as coating with metal nanoparticles, or forming composites with carbon materials (mainly graphene). An important method for reducing recombination and extending light absorption by semiconductor materials into the visible part of the solar spectrum is to form composites of two or more materials with photocatalytic properties [5].

This work discusses the synthesis, optical and photoelectrochemical behavior of titania nanotube arrays modified by Ti-Fe₂O₃/In₂O₃ composite. As expected, obtained photoanode shows the highest photocurrent density of 0.5 mA/cm² at 0.5 V vs. Ag/AgCl(3M KCl), which is nearly 5 times higher compared with pure TiO₂ nanotubes.

This work is financially supported by The National Centre for Research and Development via grant no LIDER/15/0088/L-10/18/NCBR/2019 (Integrated prototype of a photo-supercapacitor for energy storage obtained as a result of solar radiation conversion).

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Keywords

Nanotubes, photoelectrochemistry, water oxidation

P2.42

Effects of sputtering pressure and oxygen partial pressure on the photodetection performance of amorphous Ga₂O₃-based UV photodetector

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Abstract

The realization of commercial application is still a big challenge for Ga₂O₃ solar-blind UV detector. The coupling of Ga₂O₃ with Si substrate shows great promise to circumvent this issue due to the high integration of Si material. Compared with crystalline Ga₂O₃ grown under high temperature condition, amorphous Ga₂O₃ (a-Ga₂O₃) hosts the facile fabrication process, which makes it as an outstanding candidate in the application of solar blind UV detectors. In this work, the growth parameters including sputtering pressure and oxygen partial pressure were tailored to improve the quality of a-Ga₂O₃ film. It can be seen that the optimal parameters are 100%Ar atmosphere and working pressure of 20 mtorr. The Au/Ti/a-Ga₂O₃/Ti/Au structure is proposed to fabricate the metal-semiconductor-metal (MSM) photodetector, which exhibits excellent photodetection performance of responsivity, external quantum efficiency and detectivity up to 2470 mA/W, 1204.7% and 2.55×10¹² cm HZ^{1/2} W⁻¹ under 254 nm @30 V, respectively. Furthermore, the a-Ga₂O₃-based photodetector has a rapid response speed ($\tau_r/\tau_d=0.08$ s/0.157 s). These excellent photodetection performances are attributed to the increase of internal gain in a-Ga₂O₃ film, which results from the existence of more oxygen vacancies. Our findings offer a promising strategy to make the a-Ga₂O₃ based solar-blind UV detector with high integration and production in batch for commercial applications.

Keywords

Amorphous Ga₂O₃, Si substrate, Growth parameter, Solar-blind UV detector

P2.43

X-ray Photoelectron Spectroscopy characterization of the improved polymer electrolyte–Li metal interface on high-voltage solid-state batteries with Li-based additives inspired by the surface chemistry of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

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Abstract

Solid State Lithium Metal Batteries (SSLMBs) are attracting increasing attention as promising candidates for high-energy-density devices with eliminated safety concerns. They use Li^0 as anode, considered the ultimate replacement for the state-of-the-art graphite anode currently employed in Lithium Ion Batteries (LIBs) for the next generation of rechargeable batteries. However, the strongly reducing nature of lithium metal causes poor stability and low coulombic efficiency in lithium metal batteries (LMBs). Moreover, the growth of Li dendrites during cycling leads to short circuit and catastrophic failure in the cell. The lack of stability of Li metal and the propagation of dendrites are still outstanding challenges to be addressed for practical applications requiring extended cyclability.

The formation of a robust and stable solid-electrolyte-interphase (SEI) that protects electrolytes against Li metal and stabilizes Li metal anode is mandatory for the successful development of LMBs and concretely SSLMBs.

Herein we present an improved SEI driven by additives for a high-voltage Li metal cell using $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ active material (NMC622) and poly(ethylene oxide) (PEO) based electrolyte mixed with lithium bis(fluorosulfonyl)imide (LiFSI) salt. The addition of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet to form a composite electrolyte demonstrated a beneficial effect for cell cycling stability. Inspired by the improved interface of ceramic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet and Li metal and previous knowledge of favorable SEI forming species, various additive candidates were selected. Among them, LiOH demonstrated a relevant improvement on the cycling performance.

X-ray photoelectron spectroscopy showed that the addition of LiOH results in an SEI enriched in LiF in the inner part, as well as N-SO₂- environments (with S-F cleaved bond), while that without LiOH is richer in more reduced sulfur and nitrogen species, probably indicating a higher electrolyte reduction/degradation.

Keywords

Solid Electrolyte Interface, X-ray Photoelectron Spectroscopy, Solid-State Li metal batteries, Li additives

P2.44

Characteristics of electron beam vapour deposited doped-zirconia electrolyte coatings for SOFCs

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Abstract

Doped zirconia exhibit improved thermal and chemical stability, good mechanical properties, superior electrochemical characteristics and a low cost making it as a promising material for many different applications, in particular, solid oxide fuel cells, thermal barrier coatings, oxygen gas sensors, etc.

Among zirconia-based materials scandia doped zirconia (ScSZ) is the most auspicious material for IT-SOFC applications. The enhanced ionic conductivity occurs due to the stabilized cubic structure of zirconia at low temperatures and the increased concentration of oxygen vacancies. The cubic zirconia phase in these materials changes to a rhombohedral phase at a time of cooling to 500–700°C, and significantly lower the ionic conductivity. To overcome this shortcoming, co-doping with other oxides is usually applied. Yet, structural, morphological, and electrical properties of the electrolytes for IT-SOFCs are dependent not only on chemical composition but also on the preparation techniques.

This study provides a comprehensive investigation of scandia stabilized zirconia co-doped with alumina (ScAlSZ) or ceria (ScCeSZ) formed by electron beam vapour deposition which allows to control the thickness the formed thin films as well as the microstructure of the thin film. The influence of technological parameters, co-dopants and their concentration on the phase distribution, microstructure, and ionic conductivity was investigated.

The correlation between ionic conductivity and changes in the phase distribution as well as the microstructure of the coatings was observed. It was found that co-dopants, their concentration and technological parameters influence ionic conductivity. The highest ionic conductivity of 4.52 Sm^{-1} at 800°C was achieved for the ceria co-doped ScSZ while alumina co-doping provides a lower conductivity due to the crystallographic phase and structural changes.

Acknowledgments. This project has received funding from European Regional Development Fund (project No 01.2.2-LMT-K-718-01-0071) under grant agreement with the Research Council of Lithuania (LMTLT).

Keywords

electron beam vapour deposition, scandia stabilized zirconia (ScSZ), thin films, ionic conductivity

P2.45

Influence of nitrogen functional groups on the inhibition of the hydrogen evolution phenomenon in carbon materials.

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Abstract

Carbon felt (CF) treatment with diethylenetriamine introduced nitrogen functional groups able to lower the hydrogen evolution reaction (HER). The treatment of CF samples (1.5 cm x 2.0 cm) made use of a mixture containing 75 mL of diethylenetriamine and 25 mL of anhydrous ethyl alcohol and re-fluxed at 80 °C for 4 hours. Treated samples were washed with DI water and dried at 60 °C for 1 hour. Pb electrodeposition process followed in a conventional three-electrode setup including CF and CF/N as working electrodes, Ag/AgCl (saturated) as reference electrode, and a lead foil as a counter electrode. The process starts with a cyclic voltammetry (CV) test in a potential window of -1.0 to 0.5V at a sweep rate of 0.01V/s to identify the lead reduction potential at the working electrode. Pb electrodeposition by the chronoamperometry technique came next, at the lead reduction potential, constant for 60 s. Last step was samples washing with DI water and drying in a vacuum oven for 30 minutes at 60 °C. The samples named were CF/Pb and CF/N/Pb. HER electrochemical behavior was evaluated by Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV). Additional sample characterizations were Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Spectroscopy (EDS). The cyclic voltammetry results showed that the hydrogen evolution current decrease from 1.53 A/g in the CF sample to 0.37 A/g in the CF/Pb sample and 0.20 A/g in the CF/N and CF/N/Pb samples. The LSV test showed a -0.24 V shift in onset potential for hydrogen evolution after treatment with diethylenetriamine. Therefore, the CF/N/Pb present a prospective application as an electrode for negative cells in lead-acid batteries.

Keywords

HER, Carbon materials, Nitrogen , Energy

P2.46

Investigations on SURMOF formation with varying deposition parameters

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Abstract

Surface functionalization via deposition of metal-organic framework materials (SURMOF) poses a viable method for the fabrication of functional surfaces with potential suitability for applications in sensors, optical devices or heterogenous catalysis. The mechanisms of SURMOF crystallization remain obscure though. Further, liquid phase epitaxy of SURMOFs (i.e. the successive exposition of the surface to the respective precursor solutions) usually results in distinct crystallites on the surface, which conglomerate after a specific number of deposition cycles to form closed films, strongly depending on the respective MOF-system and deposition parameters.^[1,2] Additionally, the spatial separation of the precursors can lead to side products, e.g. due to inadequate stoichiometry during reaction. We investigated the deposition of Cu(II)-paddlewheel based MOF materials (HKUST-1, Cu₂(F4bdc)₂(dabco), Cu₂(bdc)₂P) in regard to the influence of the Cu(II) source, co-solvent and process variation. Those variations open further leverage on i.a. coverage, crystallinity and orientation and give valuable insight into the crystallization process.

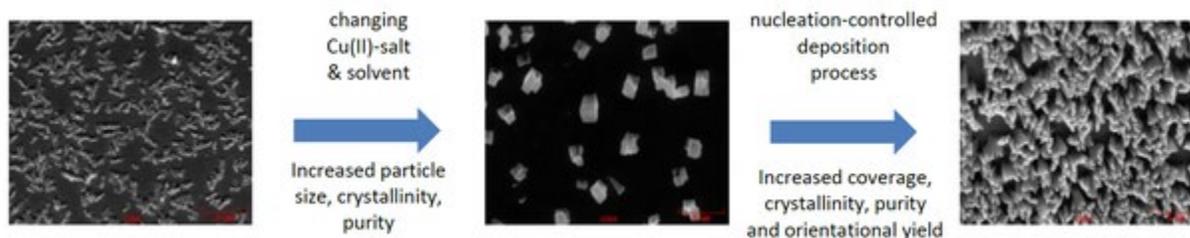


Figure 1: Scanning electron microscopic images of SURMOFs of Cu₂(bdc)₂(dp_btd), deposited with varying LPE processes. All scalebars are 5 μm.

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Keywords

Coordination polymers, Metal-organic frameworks, Cu(II)-paddlewheel, Liquid phase epitaxy

P2.47

Mechanical and tribological properties of Ni-B/boron composite coatings produced by electroless method

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Abstract

The paper presents results of research on nanocomposite Ni-B coatings with embedded particles of boron produced by chemical reduction method and their influence on the mechanical and tribological properties of produced materials. Boron was used in two forms: an alloy component and nanoparticles incorporated into the matrix.

Composite Ni-B/boron coatings and, for comparative purposes, Ni-B coatings were deposited on a steel substrate. Boron in the form of powder ($<1 \mu\text{m}$) was used as a dispersion phase. The coatings were deposited from a bath at different concentrations of dispersion phase, namely 0.1; 0.5; 1.0 g; $1.5\text{g}/\text{dm}^3$. The deposition process was carried out at constant stirring speed of 100 rpm, bath temperature of 363 K, and deposition time of 90 minutes. The paper presents the characteristics of the used boron. Results of morphology and surface topography (SEM) as well as the structure (XRD) of the produced coatings are presented. The mechanical properties of the produced coatings were tested by the Depth Sensing Indentation (DSI) method. The Vickers hardness, Indentation hardness, and Martens hardness as well as the modulus of elasticity and creep of the produced coatings were determined. The tribological tests were carried out using the ball on disc method. The test was performed under dry friction conditions. Adhesion of the produced coating to steel substrate was tested by scratch test method.

The incorporation of boron particles into the alloy nickel-boron matrix changes the morphology and topography of the surface of the produced coatings and increases the hardness and affects the wear resistance of the coating material.

Acknowledgements:

The project „New electroless Ni-B/B and Ni-B/MoS₂ composite coatings with improved mechanical properties” benefits from a €210,000 grant from Norway. The aim of the Small Grant Scheme (SGS) Call is to support applied research projects led by female scientists in technical sciences.

Keywords

composite coatings, Ni-B, electroless, mechanical properties

P2.48

Comparison of photo-, electro- and photoelectrocatalytic processes in degradation of tetracycline by titanium-based nanotube layers

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Abstract

Tetracyclines are one of the most produced and used classes of antibiotics. The extensive use of these broad-spectrum antibiotics and their limited metabolization by humans and animals have resulted in high levels of tetracycline discharge to the environmental water, thus leading to an adverse effect on ecosystems and human health. Conventional water and wastewater treatment technologies are not sufficiently effective in removing antibiotics. On the contrary, photo-, electro-, and photoelectrocatalysis are promising technologies because of their environmental friendliness, simple operation and high removal rate.

The present study compares photo-, electro-, and photoelectrocatalytic degradation of antibiotic tetracycline using titanium dioxide and titanium oxynitride nanotube catalysts prepared by anodic oxidation of titanium foil. Titanium foils were anodized at 60 V for 3 h in an ethylene glycol electrolyte with 0.3 wt % of ammonium fluoride. The anodized samples were annealed in the air to crystalize titanium dioxide into the anatase phase or in an ammonium atmosphere to form titanium oxynitride. Photocatalytic degradation of tetracycline using titanium dioxide and titanium oxynitride under ultraviolet light after 120 minutes reached 24 % and 25 %, respectively. Electrocatalytic degradation of tetracycline using titanium dioxide or titanium oxynitride as anode and platinum as cathode, reached 85 % and 83 % after 120 minutes, respectively. The sum of these two catalytic processes reached 83 % and 80 % degradation of tetracycline after 120 minutes, for titanium dioxide and titanium oxynitride, respectively. All photo-, electro- and photoelectrocatalytic reactions followed pseudo-first-order reaction kinetics. Photo-, electro- and photoelectrocatalytic kinetic constants for titanium dioxide were $1.5 \times 10^{-3} \text{ min}^{-1}$, $88 \times 10^{-3} \text{ min}^{-1}$ and $89 \times 10^{-3} \text{ min}^{-1}$, respectively. Likewise, for titanium oxynitride they were $1.3 \times 10^{-3} \text{ min}^{-1}$, $90 \times 10^{-3} \text{ min}^{-1}$, and $99 \times 10^{-3} \text{ min}^{-1}$.

Keywords

Antibiotics, Advanced oxidation processes, Titanium dioxide, Titanium oxynitride

P2.49

Photoinduced intercalation into MoO₃ films. The influence of the deposition method.

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Abstract

The concept of photointercalation is related to photoactive metal oxide semiconductors possessing a layered structure [1]. During the illumination of an n-type semiconductor with an appropriate structure e.g. MoO₃ [2], WO₃ [3], photoexcited electrons from the conduction band can be utilized for the intercalation of cations, according to the reaction:



Simultaneously, holes from the valence band have to be consumed for the oxidation reaction, e.g. water oxidation: $2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$.

Since cations are released during the anodic polarization without illumination, this phenomenon can be considered as storage of photoexcited charge carriers. Thus, direct storage of converted solar energy can be achieved within one electrode. In this case, MoO₃ is responsible for photo-absorption and energy storage, simultaneously.

Here, we have performed different methods of MoO₃ deposition. Depending on the sputtering conditions, the exposition of specific crystal planes can be achieved. MoO₃ films obtained *via* pulsed laser deposition exhibited (0k0) planes exposed. In the case of magnetron sputtering of Mo film followed by its annealing, (hk0) crystal plane is predominant. The influence of the deposition method of MoO₃ on the photoinduced intercalation was investigated using electrochemical methods, as well as novel *in-situ* Raman photoelectrochemical setup [4].

Acknowledgements

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Keywords

photointercalation, MoO₃, photoanode

P2.50

Novel family of Transition-metal intercalated Zirconium phosphonate MOFs as bifunctional electrocatalysts for OER and HER

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Abstract

With the decrease of fossil fuel reserves and the growing demand for green and sustainable energy technologies, there is a need for development of energy conversion and storage devices. Efficient sustainable electrochemical water splitting, as hydrogen fuel source, demands low-cost catalysts that don't contain rare metals. Metal organic frameworks (MOFs) are organized well defined 3d structures that can serve as catalysts due to their high surface area and porosity. Transition metal phosphonate MOFs are known OER catalyst. In this work we present a novel family of MOFs of the type $[M^{n+}][ZrCH_2(PO_3)_2F]_n$. This MOFs are easily fabricated in two steps, first the inactive $[(CH_3)_2NH_2][ZrCH_2(PO_3)_2F]$ is produced, then, cation exchange allow easy intercalation of transition metal ions that bound to the phosphonate groups, allowing versatility and quick screening of the catalytic activity of various metals.

$[(CH_3)_2NH_2][ZrCH_2(PO_3)_2F]$ MOF was synthesized using two methods, solvothermal and reflux, then several transition metals were introduced into it, serving as the M^{n+} cation. All products were characterized using SEM, XRD, FTIR, XPS, TGA, and XRF measurements. The electrocatalytic performance of the MOF was examined in basic conditions at room temperature using linear sweep voltammetry and RRDE.

MOFs made by reflux were found to be consisted of small crystals of 0.1-3mm and was generally more electrocatalytically active in comparison with the same MOFs produced by solvothermal reaction. The best reflux-made MOFs have showed good OER performance with $j=10\text{mA}/\text{cm}^2$ at over potentials of 410-500mV for Ni, Co, Fe (in a descending activity order), and Tafel slopes of 109-119mV/dec. HER performance with $j=10\text{mA}/\text{cm}^2$ was measured at overpotentials of 600-680mV for Fe, Co and Cu, (in descending activity order), with onset potentials and Tafel slopes of 162 and 187mV/dec for Co and Fe.

Keywords

MOF, OER, HER, electrolysis

P2.51

Carbon material hybrids with non-noble metal based films as electrocatalysts for alkaline water electrolysis

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Abstract

Hydrogen production by electrochemical water splitting has been recognized as one of the most promising strategies for the transition from fossil fuels to green energy sources. To use hydrogen as an attractive energy carrier, it is necessary to lower the overpotentials of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). In order to achieve this, it is necessary to develop high-effective, low-cost and easy-to-synthesis electrocatalytic electrodes.

Carbon cloth is an inexpensive, flexible and highly conductive material, that can be modified to increase the electrocatalytic activity. There are two main strategies for improvement of its electrochemical performance: modification of the electrode towards increasing the number of active sites (e.g. by electrodeposition of transition-metal-based compounds) or modification of the active centers to increase their intrinsic activity. By combining these two concepts, in this work, non-noble metal-based carbon material hybrids are created, as alternative electrocatalysts with a potential to replace currently used expensive and rare precious metals in the green hydrogen production process.

The aim of this study was to obtain electrocatalytic electrodes with high activities in both HER and OER. Carbon cloth samples were electrochemically activated to increase the electrochemically active surface area and then composite (metal/metal (hydr)oxide) coatings were applied by electrodeposition. The obtained electrodes were characterized in terms of physicochemical and electrocatalytic properties. It was studied how the change in Fe:Co molar ratios in the deposited film and the electrochemical activation procedure prior to electrodeposition impact the electrocatalytic performance of the hybrid electrodes. The highest electrochemical activity in both HER and OER was obtained for Fe:Co molar ratio of 1:3. The stability of electrodes performance was demonstrated during 24 h of operation at the current density of 10 mA cm⁻².

Keywords

iron, cobalt, electrodeposition, electrocatalysis

P2.52

Photochromic applications of titanium dioxide in various forms

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Abstract

Photochromic materials as the name implies, possess the ability to change their light absorbance when exposed to light. This allows it to be used for passive light modulation. Titanium dioxide (TiO_2) undergoes this process when exposed to UVA light under anaerobic conditions when a hole scavenger is present. Since a hole scavenger is necessary, the surrounding medium of the TiO_2 will influence the resulting photochromic effect. The highest photochromic capability can be achieved when the TiO_2 / hole scavenger interfacial area is the highest, for example, nanoparticles dispersed in a colloid. However, for practical applications, particles in a colloidal form pose many challenges, mainly leakage and solvent evaporation. Another possibility is thin films or polymer composites. However, thin films possess a comparatively low interfacial area, resulting in a low photochromic performance while TiO_2 /polymer composites have so far also shown poor performance when compared to colloids. A golden middle-point between these two could be nanoparticle dispersions in a gel form. These can retain any hole scavengers while also allowing the TiO_2 nanoparticles to be disperse enough, for efficient hole scavenging. However, most reported gels are opaque, which also undermines their usability in applications where high optical transparency is mandatory. By conducting polymerization under certain conditions, we've prepared transparent TiO_2 gels, that also possess the ability to photodarken under UVA light and slow recovery when the UVA light is turned off. The properties and compositional dependencies of the photochromic properties have been studied and are reported.

Keywords

Photochromism, Energy saving, Titanium dioxide, Photodoping

P2.53

Design of 3D-printed molecular electronics

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Abstract

3D printing technology has generated a revolution in the rapid prototyping and low-cost fabrication of 3D-printed electronic devices. However, a main drawback when using 3D-printed transducers is the lack of robust functionalization methods for tuning their capabilities. Herein, a simple and sustainable bottom-up functionalization approach is presented to tailor the capabilities of 3D-printed electronics *via* implanting molecular properties, yielding to the design of unconventional 3D-printed Molecular Electronics. On one hand, the suitability of anchoring stimuli-responsive (supra)molecular components will be demonstrated for electrically reading bistable (supra)molecular switches triggered by different inputs using electrochemical impedance spectroscopy as the output system. On the other hand, the integration of bio-recognition units (*e.g.*, enzymes, antibodies, etc.) will be discussed for the development of at-point-of-use electrochemical biosensors. Accordingly, the combination of Molecular Engineering with the emerging 3D printing technology will pave the way for the development of a new generation of 3D-printed Molecular Electronics capable of performing logical functions at the molecular level for their implementation as novel switching memories, logic gates and/or (bio)sensors.

Keywords

molecular electronics, biosensors, responsive interfaces, 3D printing

P2.54

Antimicrobial Effect of Ag Nano Island Deposited on SS316L by Physical Vapour Deposition

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Abstract

Metal nanocoatings are typically formed on dielectrics and primarily glass substrates using vapour deposition techniques such as electron beam deposition, thermal vapour deposition and other methods. With the additional structuring of these metal nanocoating, its applicability in photovoltaics can be extended by both adapting its electromagnetic properties and creating 1D and 2D photonic structures. The nanocoatings have an advantage of enhanced surface area, which also increases the surface reactivity. SS316L is one of the extensively used alloys for biomaterial and surgical tools manufacturing. Unfortunately, these implants and tools are susceptible to microorganism growth due to biofilm formation on the material surfaces and cause infections. An antimicrobial coating is therefore needed to keep the surface microbes free. Silver nanoparticles' broad spectrum bactericidal effect makes it a good candidate for nanocoating. In this study, silver nano-island are deposited on SS316L substrates using physical vapour deposition method. Metallic silver was thermally evaporated and physical vapour deposition is carried out in a vacuum environment at room temperature on SS316L substrates. Different mass of silver (7mg, 15mg, 60mg, 120mg) was evaporated and deposited as nano islands. The morphology of these nano-islands were carefully controlled in this study. This allowed the nano-islands to be highly reactive and therefore can be applied for antimicrobial application. The results show an enhanced antiviral response from Ag- coated SS316L as compared to the bare SS316L.

Keywords

Antiviral, Nano-Island, Nanocoating, Thermal evaporation

P2.56

Raman frequencies of diamond under non-hydrostatic pressure

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Abstract

The Raman frequencies of diamond subjected to non-hydrostatic uniaxial stress along the [001] and [111] crystallographic axes have been calculated with density-functional-theory methods and the results fitted to a simple analytical form. The data are analyzed in the context of the recently proposed use of the shift of the high-frequency edge of the Raman band of diamond as a pressure scale in diamond-anvil cell experiments. Combining theoretical and experimental data we are able to determine the stress state of the diamond anvil in ultra-high-pressure experiments. We find that shear stresses close to the tip of the anvil can reach values exceeding 1 Mbar.

Keywords

strain, high-pressure, Raman frequency, diamond anvil cell

P2.57

Aerosol synthesised single-walled carbon nanotubes for optoelectronic applications

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Abstract

Electrically conducting thin-film materials possessing high transparency are essential components for many optoelectronic devices. The advancement in the transparent conductor applications requires a replacement of indium tin oxide (ITO), one of the key materials in electronics. Despite being the most commonly used transparent conductive material, ITO as well as other metal oxides have several drawbacks, including limited mechanical flexibility, high refractive index and haze, limited chemical stability, and depleted raw material supply. Single-walled carbon nanotubes (SWCNTs) are one of the most promising alternative material platforms considered for transparent conducting films (TCFs) due to their excellent optoelectronic properties and unique mechanical flexibility and stretchability.

Here, we develop a novel transparent p-type flexible electrode based on SWCNTs combined with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), molybdenum oxide and SWCNT fibers. We achieved a record equivalent sheet resistance of 17 Ω /sq with a transmittance of 90% at 550 nm and a high degree of flexibility. We demonstrate that our solar cells based on the proposed electrode and hydrogenated amorphous silicon (a-Si:H) yield an outstanding short-circuit current density of $J_{sc} = 15.03$ mA/cm² and a record power conversion efficiency of PCE = 8.8% for SWCNTs/a-Si:H hybrid solar cells.

This work was supported by Council on grants of the President of the Russian Federation grant No. HШ-1330.2022.1.3 and Russian Foundation of Basic Research (project No. 20-03-00804) and Russian Science Foundation (project No. 21-72-20050).

Keywords

carbon nanotube, solar cell, doping, composite

P2.58

Wetting Studies of Smart Mechanically Tunable Lamellae

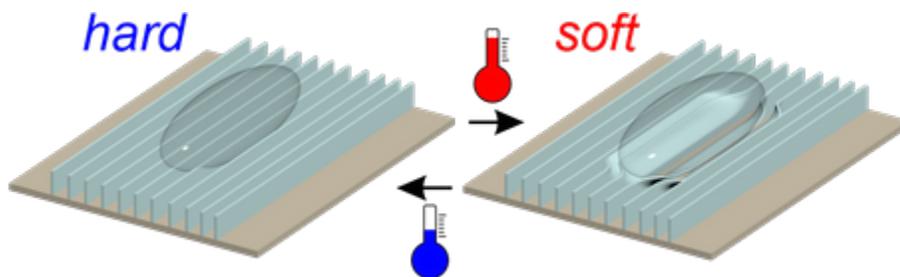
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Abstract

Various living organisms have structured surfaces with specific wettability that allows efficient adaptation to the environment and improves their survival rate. For example, the rice leaves have micro- and nanoscale structures on their surface that form a superhydrophobic surface for self-cleaning and water repellence. Bioinspiration of these natural surfaces in material science can be beneficial for different fields like biotechnology, microfluidics, sensors, etc¹. In comparison to previously reported surface patterning techniques, melt-electrowriting is a novel and solvent-free technique that is based on 3D printing and electrospinning which allows programmed deposition of polymeric microfibers². Shape memory polymers offer a very interesting combination of properties based on the switching of the mechanical properties based on the exposition to an external stimuli like temperature, light, magnetic field or others, and capability of stimuli-induced restoration of shape after deformation^{3,4}.

In the present study, we report the fabrication and investigation of wetting properties of structured surfaces with shape-memory features containing lamellae with a high aspect ratio. The wetting properties of the designed structured surfaces depend on temperature and thermal treatment history—lamellae are wetted easier at elevated temperature or after cooling to room temperature when the polymer is soft and mechanical properties are lowered. The high aspect ratio allows tuning of surface geometry not only manually, but as well by a liquid droplet and is controlled by temperature. The liquid in combination with thermoresponsive topography present a new type of wetting behavior. This feature opens the possibility to apply such topographies for design of smart elements for microfluidic devices, for example, smart valves.



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Keywords

shape memory polymer, wettability, tunable topography, thermo-responsiveness

P2.59

Degradation mechanism of prussian blue analogue electrodes in aqueous sodium-ion batteries

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Abstract

Aqueous sodium-ion batteries (ASIB) are a promising alternative to present-day lithium-ion batteries (LIB) for large-scale stationary energy storage. They are expected to overcome most of the setbacks associated with LIBs related to safety, material scarcity, and geopolitics.[1] Amongst the various types of available cathode compounds, Prussian Blue Analogues (PBA) have attracted increasing attention. PBAs share an open-framework structure with the representative formula of $A_xM^1[M^2(CN)_6]$ (where A is an alkali metal cation and M^1 and M^2 are transition metals), which allows the reversible intercalation of sodium ions. They can be sourced from sufficiently available precursors and therefore offer a low price for synthesis. In order to facilitate large-scale utilization of ASIBs, a high life expectancy of at least a decade is required for a LIB-outperforming price per kWh per cycle, which resembles several ten thousands of reversible charge-discharge cycles at the lower end.[2]

In our recent work, we investigated the degradation of PBAs using a flow-cell setup with an online inductively coupled plasma mass spectrometer. By monitoring the real-time transition metal dissolution from $Na_2NiFe(CN)_6$ and $Na_2CoFe(CN)_6$ during charge-discharge cycles, we found that the degradation mechanism is highly coupled to the electrochemical potential and current (**Figure 1a**), as well as the electrolyte anion nature and pH. Decreasing stability was found for different Na^+ electrolytes with the order of $ClO_4^- > NO_3^- > Cl^- > SO_4^{2-}$, from which we concluded that the electrode dissolution is initiated by detrimental anion chemisorption. As a result, the electrode stability can be boosted to over 10,000 cycles without degradation by a tailored electrolyte composition (**Figure 1b**).[3]

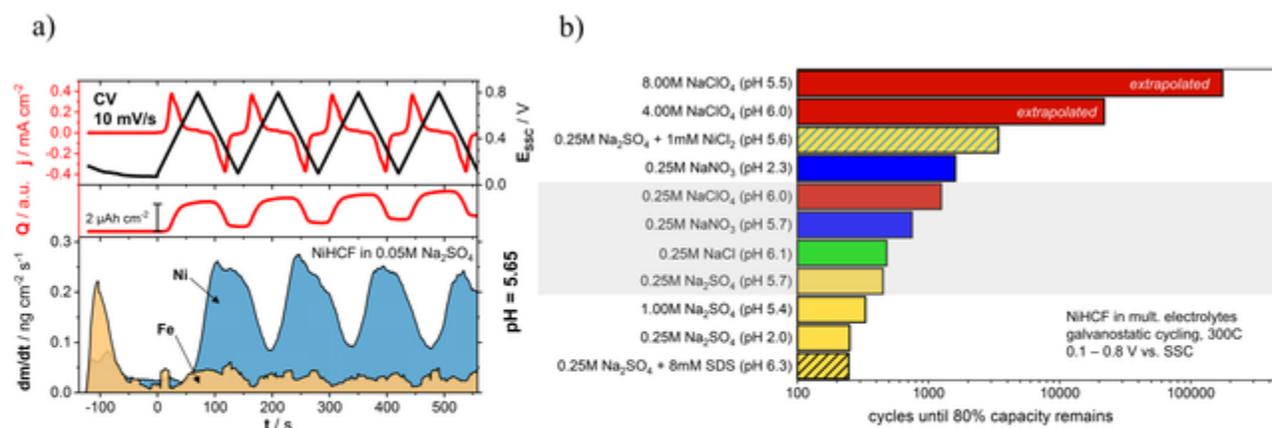


Figure 1. a) *In operando* dissolution profiles for nickel and iron from NiHCF as measured by ICP-MS during cycling. The extraction rate of Ni is highly correlated to the electrode potential and current and much more pronounced compared to Fe. b) Stability of NiHCF in several Na^+ electrolytes with varying compositions. Adapted with permission from [3]. © 2022, American Chemical Society

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Keywords

Na-ion aqueous batteries, active material dissolution, Prussian Blue Analogues, degradation

P2.60

Keratin-based Flame-retardant Textile Coatings

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Abstract

Textiles are used in many areas of daily life. They are composed of natural and synthetic polymers including cotton, polyester and their blends. Among all technical textiles, fabrics with a low flammability are often desirable. Major approaches to achieve flame retardant properties are based on environmentally harmful finishings, usually involving halogen-based compounds. The incorporation of a number of these halogenated flame retardants in combustible materials has been restricted or forbidden. Bio-based flame retardants, containing nitrogen and phosphorus, represent an eco-friendly alternative. In this study, rejected downs from goose down processing were hydrolysed to obtain keratin hydrolysate. These contain about 16% nitrogen which provides flame-retardant properties to textile substrates. Cotton, polyester, and polyester/cotton blend fabrics were coated with keratin hydrolysates using a binding agent based on ethylene-vinyl acetate copolymer. In this way, waste recycling, as a challenging aspect of industrial processes, is enabled.

Coated textiles underwent several analyses. The nitrogen content was determined by Kjeldahl method. No after flame time was observed in flame tests according to ISO 15025, while uncoated textiles burned completely down. Further experiments regarding the pyrolytic as well as the combustion behaviour were conducted by means of thermogravimetric analyses and microscale combustion calorimetry.

Keywords

Eco-friendly, Flame Retardant, Keratin, Textile

P2.61

Enzyme immobilization on textile carrier materials and their possible applications in biotechnology

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Abstract

Enzymatically catalyzed reactions provide many advantages compared to conventional chemical processes. For instance, enzymes can be used at moderate temperatures, at pH ranges close to neutral, and they are mostly safe and easy to handle. Furthermore, enzymes have a high substrate selectivity and small quantities are enough for a sufficiently high implementation rate. Another advantage is their reusability because they stay unchanged after the reaction. Therefore, the idea is to immobilize the biocatalysts on suitable carrier materials, in order to reuse them easily and improve the economical use of the highly priced enzymes. Particularly some synthetic or natural textile fiber materials such as polyester, polyamide or cotton are adequate carrier materials. They are comparatively inexpensive, their flexibility allows the use in reactors of any geometry, and they can be separated fast and without contamination of the reaction batch. Here we present various methods for the immobilization of oxidoreductases (peroxidases and laccases) on textile carrier materials and their potential application, e.g., in the gentle enzymatic degradation of food colors, the synthesis of natural flavors, or the degradation of micropollutants in sewage water.

Keywords

Enzymes, Immobilization, Textile, Biotechnology

P2.62

Silicone textured biointerfaces for breast implant applications

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Abstract

Despite the increased awareness and research funding that substantially advanced both diagnosis and treatment, breast cancer is still the most common malignancy in women diagnosed worldwide. Considering both physical and psychological impact on health-related quality of life, a large percent of women that had a unilateral or bilateral mastectomy will choose breast reconstruction. Breast implants are based on saline-filled or silicone-filled implants but both types have a silicone outer shell that will be in contact with the surrounding tissues. Therefore, it is important to underline that the silicone outer shell's characteristics will dictate many processes involved in breast implant integration within the body. As a consequence, both periprosthetic bacterial contamination and the degree of local inflammatory reactions that induce a chronic inflammatory reaction, modifications of the silicone implant, especially its surface, are aimed to increase biocompatibility and thus decrease capsular fibrosis. Therefore, in this work, we use different laser-based methods and replication for surface modification for providing a silicone-out shell with tailored multifunctional characteristics in terms of reduced bacteria attachment and modulated inflammatory reaction. Obtaining multi-architectural scales implying nano, micro, and macro-texturization was done by using replication techniques from the complex molds, and/or salt loss technique in combination with replication of the 2 D and 3D PDMS substrates. Atomic Force Microscopy, Scanning Electron Microscopy, contact angle, and surface free energy measurements were used for determining the surface topography and wettability. The responses of various microorganisms and macrophages cells to these topographies were analyzed and correlated to the surface topography and interface characteristics. It was shown that surface characteristics are highly influencing cells adhesion as well as microorganisms inhibition.

Keywords

biointerfaces, microtextured PDMS, breast implant

P2.63

New poly(N-isopropylacrylamide)-butylacrilate copolymer biointerfaces and their characteristics influence on cells behavior *in vitro*

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Abstract

Designing and obtaining new synthetic smart biointerfaces with specific and controlled characteristics relevant for applications in biomedical and bioengineering domains represent one of the main challenges in these fields. In this work, Matrix-Assisted Pulsed Laser Evaporation (MAPLE) was used for to obtain synthetic biointerfaces of poly(N-isopropylacrylamide)-butylacrilate p(NIPAM-BA) with different characteristics (i.e., roughness, porosity, wettability), and their effect on normal HEK 293 T and murine melanoma B16-F1 cells was studied. For this, the influence of various solvents (chloroform, dimethylsulfoxide, water) and fluence variation (250-450 mJ/cm²) on the morphological, roughness, wettability and chemical characteristics of the coatings were evaluated by atomic force microscopy, scanning electron microscopy, contact angle measurements, Fourier-transform-IR spectroscopy and X-ray photoelectron spectroscopy. Coatings obtained by spin coating method were used for reference. No significant alteration in the chemistry of the surfaces was observed for the coatings obtained by both methods. All p(NIPAM-BA) coatings showed hydrophilic character, with the exception of those obtained with Chloroform at 250 mJ/cm². The surface morphology was dependent on both solvent and laser fluences, being obtained from smooth surfaces to rough and porous ones. Physical-chemical and biological analysis revealed that MAPLE deposition method with fluences of 350-450 mJ/cm², when using DMSO solvent, is more appropriate for bioengineering applications due to the surface characteristics (i.e., pore presence) and to the good compatibility with normal cells and cytotoxicity against melanoma cells.

Keywords

pNIPAM-co-BA, biointerfaces , MAPLE

P2.64

Kaolinite Films obtained with the PLD and MAPLE techniques

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Abstract

In this work we propose to optimize some experimental parameters for the manufacturing/deposition of highly oriented crystalline lamellar clays films. The films were deposited by two laser-based techniques, namely Matrix Assisted Pulsed Laser Evaporation-MAPLE and Pulsed Laser Deposition-PLD. The obtained kaolinite thin films were investigated morphologically using the Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), for structural characterization using the X-ray diffraction (XRD) technique and for the chemical surface properties by X-ray Photoelectron Spectroscopy (XPS). The wetting properties of the deposited clay thin films were assessed by means of Contact Angle (CA) characterization. Thereby we can achieve hydrophobic to superhydrophilic lamellar thin films that can be prepared by using comparative deposition methods and different deposition parameters. In our experiments the MAPLE deposition method tends to obtain superhydrophilic films with the contact angles ranging between 4-8°, depending on the micro and nanostructure surface roughness. Our results showed that using the PLD method at $\lambda = 1064$ nm wavelength, a textured film was obtained in comparison with the case of $\lambda = 193$ nm in which an amorphous layer was depicted. Also, MAPLE kaolinite films showed oriented crystalline lamellar even at 5 % wt. kaolinite.

Keywords

laser processing, lamellar material, kaolinite, thin films

P2.65

Tailored surfaces characteristics obtained by laser processing approach for evaluating the *in vitro* cellular response

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Abstract

The potential of Mesenchymal stem cells (MSC) for implantology and cell-based therapy represents one of the ongoing research subjects within the last decades. In bone regeneration applications, the various environmental factors including bioactive compounds such growth factors, chemicals and physical characteristics of biointerfaces are the key factors in controlling and regulating osteogenic differentiation from MSCs. In our study we have investigated the nano and micro hierarchical biointerfaces based on ceramics and peptide self-assembling influence on the osteogenic fate of MSCs. The complex interfaces were created via a laser texturing technique. Scanning Electron Microscopy, EDAX, contact angle and surface energy of the analyzed coatings were correlated to biological response on both short and longer term (72h, respectively 28 days). Human MSC were cultured on the developed coatings and viability, proliferation and morphology were evaluated. All surfaces were shown not to exhibit toxicity, as confirmed by LIVE/DEAD assay. Micro and nanotextured ceramic interfaces exhibited an increase in osteogenic differentiation of hMSC cells, results supported by ALP and mineralization assays. This is the first report about nano and micro hierarchical biointerfaces based on ceramics and peptides directing osteogenic differentiation from hMSCs indicating potential for application in bone regeneration.

Keywords

mesenchymal stem cells, hierarchical biointerfaces, osteogenic differentiation

P2.66

Surface-enhanced Raman spectroscopy for the detection of microplastics

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Abstract

As a result of the widespread use of plastics and their fragmentation, microplastic particles (< 5 mm, including nanoplastics, < 0.1 μm) have been found in food, air, water and soil. Unfortunately, little is known about the potential harmful effects of microplastics on humans. Detection of microplastics is still challenging due to limitations of current methods, instrumentation, and particle size. In this work, surface-enhanced Raman spectroscopy (SERS) was used to detect polystyrene (PS, 350 nm) and polyethylene (PE, 1-4 μm) particles in pure water. Gold nanoparticles (Au NPs) of three different sizes were synthesized, characterized, and used as SERS active substrate for microplastic detection. The obtained Au NPs had diameters of 21, 38, and 54 nm. In addition, the largest Au NPs had a slightly uneven surface. The optimal conditions (volume ratio of sample to gold colloid, aggregating agent and its concentration) were determined. The efficient and stable SERS signals were observed on the polystyrene microparticles. The SERS method allows the detection of polystyrene microparticles at concentrations as low as 10 $\mu\text{g}/\text{mL}$. The described method can be a useful tool for the detection of microplastic pollutants.

Keywords

Raman, SERS, microplastics, gold colloid

P2.67

Selective BTX recycling from electronic plastic wastes using catalytic pyrolysis

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Abstract

Non-catalytic and catalytic pyrolysis of two waste electrical and electronic equipment (WEEE) fractions were performed using a micro-pyrolyzer equipped with gas chromatography-mass spectrometry/flame ionization detector (PyroGC-MS/FID). The materials used as feedstock were real waste fractions with two different copper contents (low- and medium-grade WEEE) processed by Boliden Mineral AB, in Sweden, to recover copper. The aim of this research was to fundamentally study the feasibility of chemical recycling of real WEEE fractions via a pyrolysis process in parallel with copper recovery. Indeed, a pyrolysis system with an efficient recycling of chemicals from WEEE can add value to the copper metal recycling process which is currently performed by Boliden Mineral AB. Pyrolysis tests were carried out at 500 and 600 °C. Al₂O₃, TiO₂, HBeta, HZSM-5 and spent FCC were used as catalyst in in-situ configuration with feedstock to catalyst ratio of 1/5 w/w. The total mass used on the experiments was 2.25 ± 0.25 mg. In in-situ pyrolysis, catalyst and feedstock were mixed in the pyrolysis cup. The hydrocarbon mixture of benzene, toluene, and xylenes (BTX) was considered as the target product to evaluate the performance of the individual catalysts. The experimental results indicated that the zeolite catalysts of HBeta and HZSM-5 were more suitable than Al₂O₃, TiO₂, and spent FCC for selective production of aromatic hydrocarbons (in general) and BTX (in particular) from the two WEEE fractions tested. Meanwhile, the ex-situ catalytic pyrolysis of the WEEE was carried out using the HZSM-5 to investigate the effect of pyrolysis configuration on the BTX selectivity. In ex-situ pyrolysis, feedstock and catalyst were separated inside the pyrolysis cup, using a quartz wool. Although the ex-situ pyrolysis resulted in higher formation of BTX from the low-grade WEEE, the in-situ configuration was more efficient to produce BTX from the medium-grade WEEE.

Keywords

Selective BTX recycling, Electronic plastic wastes , Catalytic pyrolysis, Zeolites

P2.69

Liquid Phase Infiltration of Polymer Brushes for the Fabrication of Metal Oxide Thin Films

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Abstract

Strategies in the fabrication of coherent and scalable patterned substrates with high definition at the nanometric scale, low costs and reduced waste are in urgent demand to meet the unstoppable miniaturisation of technologies. Polymer brush-assisted methods have demonstrated an encouraging implementation potential in the microelectronics industry, featuring low temperatures (< 300 °C) and short processing times (from few seconds to hours). The methodology comprises the preparation of uniform polymer brushes, or short chain polymer monolayers, covalently tethered atop of monocrystalline Si wafers with different functionalities, customisable thicknesses and reactivities. In particular, mono-hydroxy terminated poly-4-vinyl pyridine (P4VP), polyethylene glycol (PEO) and polymethyl methacrylate (PMMA) polymer brushes have been prepared and subsequently infiltrated with different precursors of the metal oxide targets. The incoming metal cations coordinate with the functional groups in the uniformly deposited brushes which upon polymer removal result in inorganic materials that delicately reproduce the polymeric assembly. Thus, the degree of selectivity of the infiltrated metal precursor with the functional groups of the polymers coating in the activated substrate areas has a notorious impact in the quality of the resulting film. We have infiltrated the P4VP, PEO and PMMA brushes of different molecular weights with solutions of metals: Ni, Cu, In, Fe, Co and Ce in concentrations ranging from 0.1 to 2% w/w. The resulting materials have been characterised by atomic force microscopy (AFM), dynamic contact angle measurements, X-ray photoelectronic spectroscopy (XPS), grazing angle Fourier-Transform Infra-red spectroscopy (FTIR) and scanning electron microscopy (SEM). Our results shed light in the fundamental understanding of the physicochemical principles governing the deposition process mediated by polymer brushes, which is a scientific gap to date in the area selective deposition methods.

Keywords

semiconductor, thin layer, metal oxides, polymer brushes

P2.70

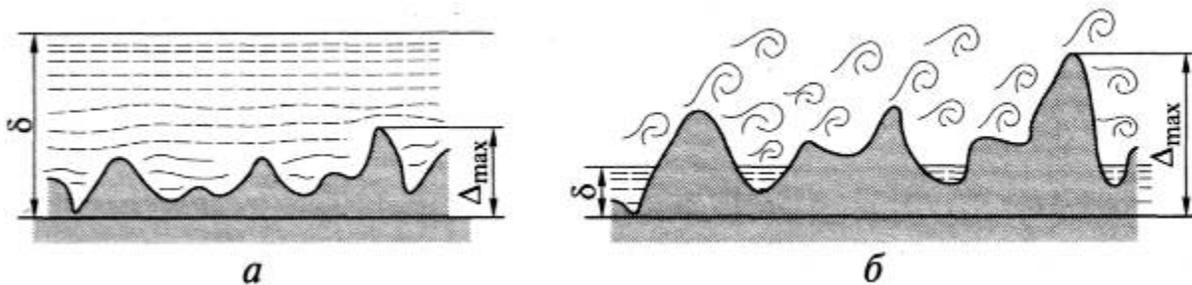
Influence of surface morphology on the hydrophilic properties of laser-irradiated titanium substrates

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Abstract

The surface of the micro- and nanostructured material shows its shape properties in bright contact with a moving liquid. The following properties of the fluid are particularly important in these processes: dynamic and kinematic viscosity, density, flow rate and the characteristic flow size, which reflect the ratio of the contact surface itself to the cross-sectional area. The situation is different if the structured surface has a more or less pronounced ability to bind or repel liquid, the extreme limits of which are called hydrophilic or hydrophobic properties. Depending on the ability of the fluid to adhere, the flow rate and the Reynolds number behind the ridges, turbulence or even cavitation zones form in the flow, which significantly affect the flow in the narrow channels.



The work offers an innovative view of the flow modelling in the vicinity of micro-and nano-structured surfaces with the Lattice Boltzmann method, where it is possible, through special regulators, to model the surface properties to attract fluid, thereby obtaining numerical solutions of Newton's fluid flow properties – front shape, turbulence, distribution of velocity.

Keywords

Titanium, Surface modification, Laser irradiation, Hydrophilic properties

P2.71

Boosting LED performance by structural disorder induced by Al₂O₃ nanofiller in MEH-PPV active layer

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Abstract

The electronics industry has been changed with the invention of organic semiconducting polymers. Their semiconducting nature, easy structure modification, solution processability, and cheap device solution fabrication make conjugated organic polymers suitable materials for LED. Nevertheless, the charge transport in semiconducting polymers is not fully described till now. Band transport, hopping or multiple trapping and release are some models to define charge transport in organic semiconductors, where atoms are strongly localized on their equilibrium lattice sites. The interplay between microstructure and electrical properties in materials that are between (poly)crystalline and amorphous is hard to be described and there exist huge differences in electrical behavior based on lattice (dis)order. Moreover, the presence of structural defects that controls non-radiative recombination is a critical factor that affects the electronic structure and optical properties of thin films. In our study, poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene-vinylene) (MEH-PPV), which is one of poly(p-phenylene vinylene) (PPV) derivative and represents a basic study material for electronic device fabrication, was used. We demonstrate the improvement of the optical and electronic properties of MEH-PPV using Al₂O₃ (Aluminum oxide nanowires) in the MEH-PPV polymer matrix. The addition of nanofiller results in the creation of new energetical states due to the deterioration of the structural order of polymer chains. These new states work as charge carrier traps thus they improve the charge carrier balance. These findings are supported by strongly increased electroluminescence of prepared LED devices, in which the active layer was MEH-PPV/Al₂O₃ nanoparticles.

Acknowledgment: The work was supported by Internal grant agency of the Tomas Bata University in Zlin, project number IGA/CPS/2022/002.

Keywords

Al₂O₃ Nanowires, MEH-PPV polymer, Thin composite films, PLED

P2.72

Towards 3D determination of the surface roughness of core-shell microparticles as a routine method for quality control by scanning electron microscopy

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Abstract

Core-shell (CS) particles have been increasingly used for a wide range of applications due to their unique properties by merging individual characteristics of the core and the shell materials. The functionality of the designed particles is strongly influenced by their surface roughness. Quantitative evaluation of the roughness of CS microparticles is, however, a challenging task for Scanning Electron Microscopy (SEM).

The SEM images contain two-dimensional (2D) information providing contour roughness data only from the projection of the particle in the horizontal plane. This study presents a practical procedure to achieve more information by tilting the sample holder, hence allowing images of different areas of a single particle to be recorded at different orientations under the same view angle. From the analysis of these images, quasi three-dimensional (3D) information is obtained.

Three types of home-made particles were investigated: i) bare polystyrene (PS) particles, ii) PS particles decorated with a first magnetic iron oxide (Fe₃O₄) nanoparticle shell forming CS microbeads, iii) PS/Fe₃O₄ particles closed with a second silica (SiO₂) shell forming core-shell-shell (CSS) microbeads. A series images of a single particle were taken with stepwise tilted sample holder up to 10° by an SEM with high-resolution and surface sensitive SE-InLens® mode.

A reliable analysis tool has been developed by a script in Python to analyze SEM images automatically and to evaluate profile roughness quantitatively, for individual core-shell microparticles. Image analysis consists of segmentation of the images, identifying contour and the centre of the particle, and extracting the root mean squared roughness value (RMS-RQ) of the contour profile from the particle projection within a few seconds.

The variation in roughness from batch-to-batch was determined with the purpose to set the method as a routine quality check procedure. Flow cytometry measurements provided complementary data. Measurement uncertainties associated to various particle orientations were also estimated.

Keywords

core-shell particles, image analysis, roughness, scanning electron microscopy

P2.73

Role of polyethyleneimine on the crystal orientation of ZnO nanorods for photoelectrochemical water splitting

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Abstract

The photoelectrochemical (PEC) water splitting is an ever-growing strategy for producing renewable fuels in addition to solving the worldwide energy demand. As photoanode in PEC cell, ZnO nanorods with controlled crystal orientation were grown on transparent conductive glass substrates via facile hydrothermal method. In order to investigate the influence of crystal orientation on the PEC performance of ZnO nanorods, the polyethyleneimine (PEI) as a cation surfactant concentration was varied in the growth solution. The lateral growth of ZnO nanorods decreased as the content of PEI was increased, resulting in the formation of irregularly aligned ZnO nanorods. The resultant ZnO nanorods exhibited non-monotonic PEC performance, which maximized for the sample fabricated from the solution with highest PEI content. This PEC activity improvement was assigned to the differences such as film surface area and charge transport properties.

The work was supported by the grant of the Ministry of Education, Youth and Sports of the Czech Republic No.: LTT20010 within the framework of the program INTER-EXCELLENCE.

Keywords

ZnO, PEC, crystal orientation, Polyethyleneimine

P2.74

Replication of biopolymer microstructures

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Abstract

Recent research shows that cell cultures grow much better on a specifically structured surface compared to a surface without modification. The specific structure and various shapes of the resulting matrices allow the cells to have different growth rates in three-dimensional space. By those findings especially tissue engineering has been dramatically impacted. Such structured surfaces are most often made by electron beam lithography (EBL) or a focused ion beam (FIB) lithography. Both procedures are based on knocking out the atoms from a fabricated surface by highly energetic particles such as electrons, respectively gallium, or xenon ions. Although ion lithography is more time-consuming than EBL, ion patterning has the clear advantage of no additional processing of the pattern. This advantage results in more precise and complex shapes that are desirable for cell adhesion research. Since material processing using ion beam nanolithography has achieved satisfactory precision, the fabrication of large patterns has become another challenge to be overcome. More complex matrix structures, such as fractal patterns, have not yet been tested for specific cell growth. Fractal patterns appear to be a particularly interesting choice, as they are commonly found in both living and inanimate nature: snowflakes, lightning, fjords, river nets, blood vessels, veins, or some plant flowers. Lithographically structured matrices can serve as a model for the subsequent replication process to various biopolymers such as poly(L-lactide) [PLLA]. There are several approaches for preparing such biopolymers, for example, heating a preformed polymeric film to a temperature that is between the glass transition temperature and the melting point of the polymer leading to films of up to about 50 μm in thickness, while retaining their mechanical properties. The modified polymers are then used as a substrate for the growth of various cell types in tissue engineering.

Keywords

replication, surface morphology, ion lithography, thermal annealing

P2.75

Effect of synthesis parameters on the surface properties of carbon spheres

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Abstract

Highly microporous carbon spheres intended for use in CO₂ adsorption research were prepared by using a modified one-beaker Stöber synthesis in the presence of various alcohols. In particular, the influence of alcohol concentration alterations was investigated for ethanol, isopropanol, and butylene glycol. Comparisons were mainly made concerning different values of [w/a] indicating a volumetric concentration of water to alcohol in an environment of polycondensation.

Resorcinol and formaldehyde were used as carbon precursors, ammonia as a catalyst, which after 24h long stirring led to phenolic resin spheres. The contents of the beaker were then treated inside the microwave reactor under a pressure of 20atm for 15 minutes and then obtained material was dried at 80°C for 24h. The dry material was then carbonized at 700°C.

SEM coupled with statistical analysis of obtained carbon spheres (CS) shown, that with the increase of the carbon chain in the solvent alcohol, the ratio [w/a] necessary for the complete formation of the spheres also increases. It is also possible that with the lower the [w/a] ratio small spheres will agglomerate more intensively, with the possibility of producing additional, non-spherical carbon structures with increased brittleness. BET surface areas for materials with [w/a] = [1; 3] measured for isopropanol CS is included in the range between 370.437 m²/g and 511.864 m²/g.

Analysis of butylene glycol suggest, that an increased amount of hydroxyl groups in the environmental alcohol may result in a reduction in the diameters' distribution of the carbon spheres, but significantly raise the average pore radius of the sample, from $1.12 \cdot 10^1 \text{ \AA}$ for isopropanol [w/a] = 2,5 version to $3.65 \cdot 10^2 \text{ \AA}$ of a butylene glycol one.

Acknowledgments: The authors acknowledge the support from the National Science Centre with OPUS 17 grant 2019/33/B/ST8/02044

Keywords

Carbon spheres, CO₂ adsorption, Hydrothermal treatment, Microporosity

P2.76

Effect of salt bath nitriding temperature on the fretting wear behavior of 2.25Cr-1Mo steel in liquid sodium

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Abstract

In this study, salt-bath nitriding of different temperatures was used on 2.25Cr-1Mo steel. The effects of salt-bath nitriding temperature on the fretting wear behavior of 2.25Cr-1Mo steel in liquid sodium were investigated. The results show that salt-bath nitriding can form a multilayer structure with higher hardness on the surface of 2.25Cr-1Mo steel. The hardness of QPQ 590 is lower than that of QPQ 550, because the excessively high nitriding temperature causes premature failure of the nitriding layer. QPQ 550 showed better wear resistance, and the untreated sample has the largest wear volume. Wear of nitrided samples in liquid sodium at elevated temperature is the result of a synergy of mechanical forces, thermal effects and sodium corrosion. The possible fretting wear mechanism of salt bath nitriding samples in liquid sodium was discussed.

Keywords

2.25Cr-1Mo, salt bath nitriding, liquid sodium, fretting wear

P2.78

Effect of modification of nanocomposites by ionic liquid for sorption in aqueous environment

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Abstract

Ionic liquids are promising green solvent and large possibilities of their use depend on the type of ionic liquid. Zeolites have been studied for a long time mainly for catalysis but zeolites are also a good sorbent. It was published by our workgroup that graphene oxide is a great material for preparation of nanocomposites where it plays role as active component for sorption. The interest was to develop selective sorbent or sorbent with very high sorption capacity. Therefore, the zeolite was used for preparation of nanocomposite with graphene oxides. The interesting effect of modification by ionic liquids was studied for heavy metals and radionuclides. The inorganic-organic system proposes the possibility to offer more sorption mechanisms. The inorganic part of zeolite contains defined size of pores and the organic part could be connected by ionic interaction. All nanocomposites were characterized for their structural and morphologic properties.

Keywords

graphene, ionic liquid, sorption, zeolite

P2.79

Carbon and zeolite based composites for radionuclide and heavy metal sorption

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Abstract

Water pollution by heavy metals and radionuclides is a several issue. Zeolites have been investigated for some time as sorbents of heavy metals. Since graphene oxide was already reported promising for radionuclide sorption, we developed composite materials containing both zeolite and graphene oxide. The composites contained graphene as well. Moreover, one of the composite samples contained carboxylated graphene oxide. The following zeolite types were used: A, P and Y. The zeolites were synthesized by a hydrothermal method from metakaoline. The composites were characterized by X-ray powder diffraction, Raman and FTIR spectroscopy. Morphology was observed by scanning electron microscopy. The developed materials were tested for sorption of selected radionuclides and heavy metals. Sorption of heavy metals was determined by atomic absorption spectroscopy.

Keywords

graphene, zeolite, composite, sorbent

P2.80

Cyclic stability tests based on BTX gaseous air compounds removal utilizing AgNPs/TiO₂/ACF filtering felt cloths

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Abstract

Short-term exposure to BTX pollutants may irritate the eyes, skin, or respiratory tract, while prolonged exposure is associated with an increased risk of cancer, liver and kidney damage, and nervous system dysfunction.

TiO₂/AgNPs photocatalysts (containing ca. 3, 5 and 10 wt.% of AgNPs) were obtained by wet impregnation, including chemical reduction of silver ions to nanoparticles and calcination at 300-700°C (4 h, Ar flow). For non-calcined photocatalysts, the increased AgNPs content caused the decrease of the specific surface area (S_{BET}) and pore volume compared with unmodified TiO₂ (supplied from Grupa Azoty Zakłady Chemiczne "Police" S.A. Poland). For a calcined group of powders, regardless of the AgNPs content, similar changes in morphology and structural properties were noticed. The preparation of Ag/TiO₂/ACF composite cloths utilising commercial 2-3 mm thickness ACF felt (provided by Eurocarb, UK). About 50 mg of AgNPs/TiO₂ suspended in ethanol were dispersed onto the surface of ACF felt fragments (3.5 x 3.5 cm) via the spraying process.

High SBET of pristine ACF cloth decreased due to covering of carbon fibres with AgNPs/TiO₂ and partially clogging the ACFs micropores. The photocatalytic properties of the AgNPs/TiO₂/ACF filtering cloths were determined by performing the photocatalytic tests utilizing the gaseous mixture of BTX air compounds (5 ppm each in air). The presence of AgNPs was one of the essential factor influencing the BTX removal. The BTX photoremoval studies tested in 5 consecutive adsorption/photooxidation cycles showed the improved BTX removal rate for all AgNPs/TiO₂-modified ACFs. No effect of the AgNPs content on the BTX photoremoval rate was found (with similar satisfactory results). The highest BTX photoremoval rate was calculated for all AgNPs/TiO₂_700/ACF cloths due to the best chemical stability of photocatalysts.

Acknowledgements: This work was supported by the National Centre for Research and Development, Poland under project No. LIDER/31/0115/L-9/17/NCBR/2018.

Keywords

photocatalysis, TiO₂-coated ACF felts, air purification, BTX photoremoval

P2.81

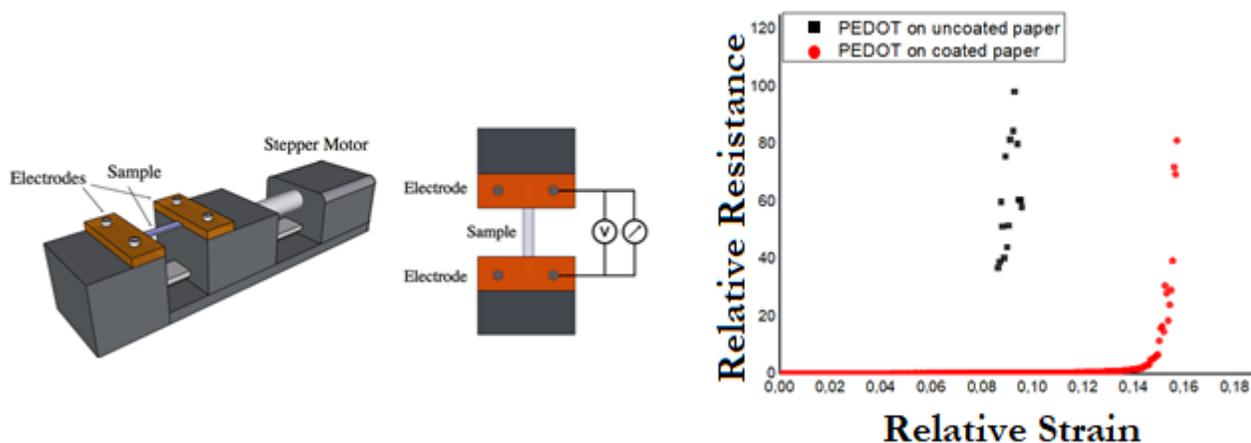
Engineered paper surface for the fabrication of large area electrodes.

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²University of Rome Tor Vergata Department of Electronic Engineering, Roma, Italy

Abstract



Flexible electronics have become quite widespread in the last decade. The recent progress achieved concerning organic semiconductors, amorphous silicon and conductive polymers allowed an enormous step forward in the production of increasingly performing devices, especially in applications where folding, bending, and stretching is required. However, many challenges remain open. Given the environmental crisis that our planet is facing, the use of sustainable materials, and less time and energy consuming fabrication methods, has become crucial. In this context, the fabrication of flexible, light weight, large area electrodes on paper, using low-energy and scale-up techniques seemed relevant. In this work, we report the morphological, electromechanical characterization and the electronic performances of large area PEDOT:PSS electrodes fabricated on coated paper. In particular, different cellulose-based polymeric coatings were rheologically characterized and tested. Aiming to optimize the spreadability of the coating and the layer homogeneity, according to rheological data, we investigated and applied solutions at various viscosities and concentration for each type of cellulose. Paper was coated with one to three layers of cellulose polymer solution, in order to attain a homogeneous surface for a regular deposition of the polymeric electrode material. Moreover, barrier properties to moisture were investigated and the best coating solution in terms of morphology and barrier properties was chosen as paper coating for the fabrication of the electrode.

The electromechanical properties of the electrodes fabricated on this improved paper surface were characterized, proving a decreased resistance and a better response of the electrode under mechanical

and environmental stress, if compared to the one realized on uncoated paper. Thus, such engineered paper surfaces obtained with an in-house sustainable method, are a good candidate for the fabrication of low-cost organic electronic devices for daily bases applications and wearable devices.

Keywords

flexible electronics, conductive polymer electrode , biopolymer coating, large area electrode

P2.82

Exploiting surface properties of electrically conductive xanthan gum - polyaniline composites to produce biocompatible scaffolds for cells growth and proliferation

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Abstract

The continuous progresses in biomedical technologies are triggering the research towards the exploration of novel materials to achieve further development in tissue engineering applications. A lot of efforts are being focused on manufacturing scaffolds for the cells' proliferation and differentiation to end the shortage and drawbacks of donated tissues and organs. The requirements of biocompatibility, electrical conductivity and proper mechanical properties are addressing the attention of the scientific community on conductive polymers (CPs) as inclusions of bio-composites materials. In fact, the electrical and ionic conductivity provided by these fillers could mimic the cellular environment in the final composite as to actively improve the material-cells interface, and to enhance cell interaction and growth.

In this context, our research is focused on the design, synthesis and characterization of novel scaffolds based on xanthan gum polysaccharide (XG) and polyaniline (PANI) CP. By allowing the formation of a three-dimensional network that mimics the morphology, structure and functionality of a native tissue, the polysaccharide component would ensure biocompatibility and biodegradability. On the other hand, thanks to its different redox states, PANI would guarantee efficient charge transfer and ionic conductivity properties ideal for simulating the biological electrical environment of tissues.

The samples are prepared by an in-situ polymerization of the aniline monomer inside the XG matrix and successively characterized by means of different techniques. The molecular structure is studied by different spectroscopy methods: UV-Vis, Raman spectroscopy, AT-IR and XRD, while samples conductivity is tested by using the four-probe technique. Cell viability is evaluated by fluorescence microscopy whereas Variable-Pressure Scanning Electron Microscopy images of cells-seeded samples allow us to analyze both the surface morphology of the composite and of the cells in the hydrated state.

Keywords

Tissue Engineering, Conductive Polymer, Composites, Biomaterial

P2.83

Photodegradation of ciprofloxacin by zinc oxide nanoparticles and cobalt oxide quantum dots

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Abstract

The antibiotic ciprofloxacin (Cipro) is an effective treatment for some bacterial infections. Due to the indiscriminate use and accumulation in the environment, it is considered an emergent pollutant. Some routes of the degradation of Cipro are known, such as chemical, physical and biological ones, yet photocatalysis is the most useful and reliable one. The photocatalytic response is faster and more effective in combination with metal oxide nanoparticles. The present study used zinc oxide nanoparticles and cobalt oxide quantum dots to promote degradation, mainly because of their capacity to produce reactive oxygen species under UV-Visible light. UV-visible spectrophotometry and Fourier Transform Infrared (FTIR) spectrophotometry showed the ciprofloxacin degradation, and microbiological tests showed the inactivation of the antibiotic, which may prevent the emergence of resistant strains.

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Keywords

degradation of emergent pollutant, ciprofloxacin, zinc oxide nanoparticles, cobalt oxide quantum dots

P2.84

Adsorption-based CO₂ capture utilizing TiO₂-modified carbon spheres

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Abstract

Continuous increase in CO₂ emissions into the atmosphere is forcing the search for new methods of removing it to slow climate change. One of these methods involves sorption and photoreduction on TiO₂-based composite materials [1].

The purpose of this study was to obtain TiO₂-modified carbon spheres and confirm their utility in the CO₂ adsorption process, comparing preparation methods. TiO₂ was prepared via the sol-gel method using titanium (IV) isopropoxide as titania precursor. The pH regulation step was used to obtain samples with pH values of 3 and 10. As-prepared powders were pre-dried at 100°C, and after this, TiO₂ photocatalysts were calcined at 400 or 700°C. Carbon spheres were obtained via Stöber method, with resorcinol and formaldehyde as substrates. Composite materials were synthesized in two ways:

(1) with the addition of TiO₂ at the polycondensation stage and composite calcination at 700°C,

(2) with the mechanical mixing of TiO₂ with previously prepared carbon spheres and without final calcination.

In both cases, atomic ratio of carbon-to-titanium reached 2:1. Obtained materials were characterized by a wide range of sphere sizes, from 600 nm to 1.5 μm. TiO₂-modified carbon spheres characterized with lower specific surface area than reference CS material. This is due to the blocking of micro- and ultramicropores by TiO₂ nanoparticles and their agglomerates deposited on surface of the spheres. Regardless of the preparation of the composites and the type of TiO₂ added, sorption capacity for CO₂ was on average 2 and 1.5 mmol/g (1 bar, 0 and 25°C, respectively).

Acknowledgements: The research leading to these results received funding from the Norway Grants 2014–2021 via the National Centre for Research and Development under the grant number NOR/POLNORCCS/PhotoRed/0007/2019-00.

[1] Yin, Wen-Jin, Wen, Bo, Ge, Qingxia, Li, Xi-Bo, Teobaldi, Gilberto, Liu, Li-Min (2020). Dalton Transactions 49 (37). 12918 - 12928.

Keywords

CO₂ adsorption, carbon spheres, TiO₂

P2.85

Innovative washable fabric triboelectric nanogenerators for face masks against the covid-19 outbreak

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Abstract

Recently, due to the covid-19 pandemic, face masks have become a necessity. Along with this trend, the potential of masks as a wearable device is receiving new attention. And meanwhile, the triboelectric nanogenerators (TENGs) that have been newly emerging in the field of energy harvesting over the past 10 years is being studied a lot of as energy source or sensor. However, although studies for TENGs are diverse and numerous, few studies to focus on combination of fabric-TENGs and face masks and reusability have been published. In this study, we studied face masks made of fabric-TENGs that can maintain electrical performance even under daily life stress such as washing. The electrical characteristics and stability of fabric TENGs were evaluated under various washing condition such as the number of washes, washing time, and washing temperature. For fabric, flash-spun nonwoven and meltblown nonwoven were selected. Flash-spun nonwoven is a fabric consist of high-density polyethylene fiber and meltblown nonwoven is a fabric consist of polypropylene fiber. The maximum output voltages of TENGs before washing exhibited 120 V with flash-spun nonwoven and 278 V with meltblown nonwoven, and after washing those were changed to 105 V and 155 V, respectively. The maximum output voltages decreased by 12.5% for flash-spun nonwoven and 43.8% for meltblown nonwoven. Although the output voltage of TENGs with flash-spun nonwoven is lower overall than those with meltblown nonwoven, the former device was much more stable under washing stress.

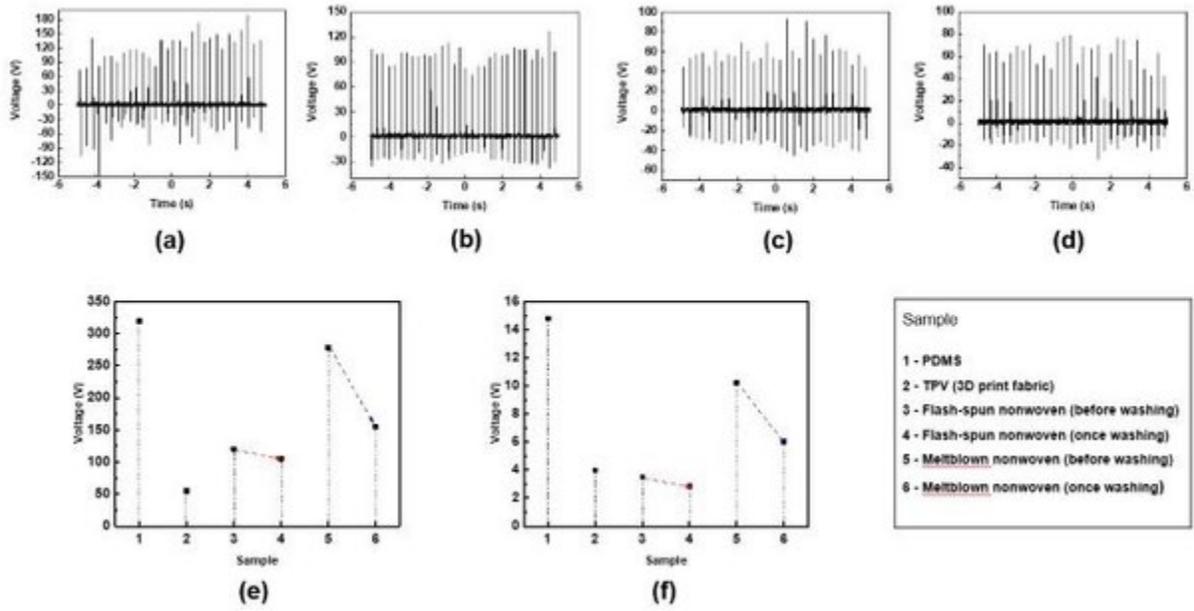


Figure 1. Output voltages of meltblown nonwoven (a) before washing, (b) after washing and flash-spun nonwoven (c) before washing, (d) after washing with high pressure (23 N), and (e) the maximum peak to peak voltages of TENGs made of different kinds of sheet with high pressure and (f) low pressure (2.2 N)

Keywords

Triboelectric nanogenerator, Energy harvesting, Face masks, Reusability

P2.86

Novel deep eutectic solvents (DESs) based stationary phases for gas chromatography

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Abstract

Deep eutectic solvents (DES) are a new class of materials of high popularity in science. They are characterized by a substantially lower melting point compared to that of pure components. This development allows to use new classes of organic compounds normally in solid state under normal conditions as solvents as well as active components of liquid sorptive media[1-2].

This paper presents application of DESs as novel class of stationary phases for gas chromatography. Two different DESs having advantageous properties for GC were described. A first DES was obtained by mixing tetrabutylammonium chloride (TBAC) as a hydrogen bond acceptor (HBA) with heptadecanoic acid being a hydrogen bond donor (HBD) in a mole ratio of HBA:HBD equal to 1:2. Its characterization by Rohrschneider – McReynolds constants revealed that this DES is a stationary medium polarity phase having interesting unusual in respect to commercial stationary phases selectivity towards alcohols [3]. Second DES-based stationary phase was obtained using a protonated L-proline and xylitol. This phase revealed to have high polarity and great selectivity towards alcohols and pyridine derivatives.

Details on DES and GC columns preparation are presented along with detailed characterization of these phases, including types of intermolecular interactions between DESs and separated solutes. Examples of separation applications in respect to volatile organic compounds are also discussed.

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Keywords

Deep Eutectic Solvents (DES), chromatography, stationary phases, volatile organic compounds

P2.87

Selective synthesis of cobalt modified molybdenum nitrides deposited on activated carbon

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Abstract

Among known molybdenum nitrides, the nonstoichiometric cubic γ -Mo₂N and the stoichiometric hexagonal δ -MoN are currently the most sought after¹. Hexagonal δ -MoN is emerging material for the design of novel electrochemical sensors for drugs², surface-enhanced Raman scattering (SERS) substrates³, and electrodes in Li-ion batteries⁴. Both molybdenum nitrides are also studied in electrocatalytic water splitting⁵. However, the progress in the application of functional materials containing molybdenum nitrides is limited by rough synthesis conditions⁶. Also, selective synthesis of γ -Mo₂N and δ -MoN is highly challenging¹.

In this study, we have examined the facile synthesis route of molybdenum nitrides recently reported by Song et al.¹. We studied structural transformations that occur during the temperature-programmed reaction of the oxidic precursor CoMoO₄ deposited on activated carbon with ammonia, with the use of in-situ XRD and thermogravimetry. We have examined the surface composition and morphology of the obtained materials with the use of XPS, SEM and BET measurements. Modification of the temperature program results in the obtaining of the product containing δ -MoN and metallic cubic Co. The change of the temperature of the reduction-nitridation process and reaction time enables further tailoring of the phase composition, as well as the morphology of the final product.

The scientific work was financed by The Polish National Centre for Research and Development, grant „Lider”, project No. LIDER/10/0039/L-10/18/NCBR/2019.

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P2.88

The metal surface matters the enhancement of gas hydrates nucleation and growth

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Abstract

The gas hydrates formation in quiescent reactors usually proceeds only at the water-gas interface, with further growth rate decreasing by several orders of magnitude (up to complete termination). The addition of surfactants (for example, SDS) usually leads to the transfer of free water to the reaction zone due to capillary suction. A hydrate "halo" spreads around the water droplet if the hydrate growth proceeds without surfactants. This work revealed the unique effect of the metal type and its surface on the nucleation and growth of methane hydrate. The study was performed in an autoclave equipped with two sapphire windows, a microscope at -5°C, and a methane pressure of about 14 MPa. Gallium (Ga), indium (In), tin (Sn), their eutectic alloys, and mercury (Hg) were chosen as the ones in contact with water. For comparison, fluoroplastic and pipe steel were selected. As expected, methane hydrate formed only on a water droplet surface with no further growth in the case of fluoroplastic while the hydrate spread over the steel surface. The presence of water contact with Ga, In, Sn, or Hg often resulted in the growth of oriented whisker crystals and, most likely, in complete conversion of water into hydrate in a relatively short time. It should be noted that the morphology of growing crystals depends on the type of metal surface. The polycrystalline surface of In, Sn, Ga/In alloy (formed during the crystallization from a melt) and metal/alloy melts facilitated the growth of strictly oriented crystals colony (along the normal to the metal surface). On a section of metals, growth was observed either in many colonies (on indium) or random whisker crystals (on tin). Thus, the surface type has a strong influence on the growth rate and morphology of methane hydrate. Besides, indium significantly improved the hydrate nucleation.

Keywords

gas hydrates, metal surface, heterogeneous nucleation, enhanced growth

P2.89

Antimicrobial activity of modified titania photocatalysts under LED light and rotating magnetic field conditions.

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Abstract

Due to the constantly shrinking reservoirs of drinking water, new methods are sought that would allow for cheap and effective purification and treatment of water for re-consumption. A promising method is photocatalysis, as well as magnetic water purification. The combination of these methods would make it possible to obtain an efficient and ecological method of water purification. Photocatalytic disinfection consisting in the in situ generation of highly reactive oxygen species that cause the oxidation of organic pollutants and pathogenic microorganisms. The Magnetic Water Treatment (MWT) technology which involves the use of enhanced separation and adsorption of particles or materials with magnetic properties in a magnetic field.

The experiments were performed in a self-designed and constructed photoreactor with a rotating magnetic field generator. A reference strain of Gram-negative bacteria *Escherichia coli* K12 (ATCC 29425) was used in the experiments. A series of experiments were performed using metal-modified titania photocatalysts and the base photocatalyst HomoP25 in LED light and different frequency of rotating magnetic field (5 Hz, 50 Hz). The best antibacterial activity was obtained for photocatalyst 2.0Cu@HomoP25, for which the effect of full disinfection was obtained after one hour of the process using LED light and magnetic field of 5 Hz frequency. After three hours for the same photocatalyst activated by magnetic field with a frequency of 50 Hz, a similar antimicrobial activity was observed. For the other tested modified photocatalysts (2.0Ag@HomoP25, 2.0Pt@HomoP25), total reduction was obtained after three hours, regardless of process conditions. The pristine photocatalyst HomoP25 did not show high antimicrobial activity in both variants of the process. None of the tested photocatalysts showed toxic properties to bacteria in dark conditions.

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Keywords

Titanium dioxide, Pristine, Rotating magnetic field, Antimicrobial activity

P2.90

Functionalization of gold nanoparticle surface with the photosensitizer methylene blue using mercaptoundecanoic acid as a linker

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Abstract

Gold nanoparticles (AuNPs) have unique photophysical properties, making them promising materials for energy transformation, harvesting, and catalysis when conjugated to molecules. These properties come from nanoparticles surface plasmonic resonance effect (SPR). Like AuNPs, many organic molecules absorb visible light, as is the dye methylene blue (MB) case. Photochemical properties of MB are widely studied in the fields of medicine, advanced materials, bioelectronics, and energy since such properties can be modulated by dye aggregation favored by interaction with interfaces. To improve and even obtain new photochemical properties for MB by synergism with inorganic nanomaterial photophysical properties, such as surface plasmon resonance, the present study focused on the functionalization of AuNPs with the dye using 11-mercaptoundecanoic acid (MUA) as the linker. The material synthesis started with the synthesis of naked AuNPs (AuNP-NK), without coating, reducing gold ions with sodium borohydride. Nanoparticles were further functionalized with MUA to increase colloidal stability. The obtained material (AuNP-MUA) was then put in contact with an aqueous solution of the cationic dye to complete the synthesis and formation of MUA and MB-covered nanoparticles (AuNP-MUA-MB). Effective functionalization of nanoparticles was proved by UV-vis and FTIR spectra, which showed absorption bands characteristic of the materials involved, with some deviations that indicate the existence of interactions between the conjugated materials. Data obtained by DLS clearly showed an increase of the hydrodynamic radius and a more negative surface charge of AuNPs. The success of the synthesis and functionalization of AuNPs with photoactive molecule MB has been demonstrated, proving its attachment to the material and potential change in its properties. Further characterizations of AuNP-MUA-MB by electron paramagnetic resonance and X-ray excited photoelectron spectroscopy are ongoing to obtain more information about photophysical and photochemical properties of the functionalized material to establish the applications.

Keywords

Gold nanoparticles, Methylene blue, Photochemistry, Functionalization

P2.91

Design and application of polymer-core/ silica-shell particles as promising tools for multiplexed assays

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Abstract

The simultaneous detection of different analytes has gained increasing importance in recent years, especially in the fields of medical diagnostics and environmental analysis. Multiplex assays allow for a range of biomarkers or pollutants to be rapidly and simultaneously measured. Particularly suitable formats for multiplexing are bead-based assays. The beads employed need to fulfil size and density requirements, important for instance for flow cytometry, and shall exhibit a high modularity to be facily adapted to various kinds of analytes and detection systems. Core/shell particles are ideally suited in this sense because of their modularity in design and adaptability for various (bio)analytical assays. Here, polystyrene particles coated with different kinds of shells are presented, possessing features that are useful for a multitude of assay formats.

The particles in focus were coated with mesoporous and non-porous silica shells, with the possibility to introduce magnetic features to facilitate easier handling dependent on the assay format (e.g., in microfluidics). With high throughput analyses in mind, cytometric model assays were developed. Different factors such as pH or mediator salt used during shell preparation were evaluated with shell inspection by electron microscopy (SEM/TEM/EDX) being key to architectural control of the monodisperse particles. The optimized core/shell particles can be functionalized with capture biomolecules for toxins, viruses, or drugs to demonstrate particle performance. Showing how tailoring of the shell's surface area controls sensitivity and dynamic range of the assay, an antibody-based assay for the detection of mycotoxins and a multiplex assay for the determination of DNA from different human papilloma virus (HPV) lines were developed.

Keywords

core-shell particles, multiplexing, surface area control, cytometry

P2.92

Improvement of surface light absorption of ZnO photoanode using a double heterojunction with α -Fe₂O₃/g-C₃N₄ composite to enhance photoelectrochemical water splitting

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Abstract

Zinc oxide (ZnO) is one of the desirable photoelectrode materials in the photoelectrochemical (PEC) splitting of water. However, poor visible light response and high recombination rate limit its photocatalytic applications. In this study, double heterojunction was applied to improve the light absorption and decrease the recombination of photogenerated charge carriers on the surface of photoelectrode. Here, a simple hydrothermal process was proposed to fabricate the ZnO photoanode. Further, ZnO/ α -Fe₂O₃ heterojunction was synthesized using a facile and low-cost drop-casting process. When the surfaces of the ZnO nanorods were uniformly deposited with a thin layer of α -Fe₂O₃, the photocurrent increased up to 0.6 mA/cm² at 1.23 V vs. RHE under 100mW/cm² illumination after five cycles of α -Fe₂O₃ deposition on the surface of the ZnO photoanode. In addition, g-C₃N₄ nanosheets were easily loaded on the surface of the ZnO/ α -Fe₂O₃ photoanode by immersing on the prepared solution of the optimized thickness for g-C₃N₄ nanosheets. These α -Fe₂O₃/g-C₃N₄ composites could efficiently respond and utilize the photons in the visible light region, which increases the photocurrent density around 3 and 5 times more than those pure ZnO/ α -Fe₂O₃ and ZnO electrodes, respectively. In addition, the fabricated heterojunction on the surface of ZnO photoanode was investigated using time of flight-secondary ion mass spectrometry (TOF-SIMS) analysis to obtain details about depth, surface, and interface. Moreover, flat band potential (V_{fb}), donor concentration (ND), and charge transfer resistance (R_{ct}) were systematically estimated by Mott-Schottky and Electrochemical impedance spectroscopy (EIS) analyses. Finally, the results show the enhanced photocurrent density in ZnO/ α -Fe₂O₃/g-C₃N₄ photoanode, which were attributed to the increased light absorption (UV-vis) and the increase in the donor concentration (Mott-Schottky).

Keywords

Photoelectrochemical (PEC) water splitting, visible light absorption, ZnO nanorod, g-C₃N₄ nanosheet

P2.93

High-entropic alloys for electrochemical ammonia synthesis in alkaline electrolytes

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Abstract

Ammonia is essential to the global economy as a fertilizer and it is a promising fuel alternative that benefits from its high hydrogen content and easy liquefaction. Ammonia is thus a potent hydrogen storage carrier. Electrocatalytic ammonia synthesis using renewable energy is an attractive low-temperature alternative to the commonly used high-temperature Haber-Bosch process that releases CO₂ into the atmosphere, thus contributing to the greenhouse effect. The main bottleneck of this approach is the low efficiency of the available catalysts for large-scale ammonia production that does not fulfil industrial requirements. In this context, high-entropy alloys (HEAs) are emerging as potential candidates to overcome scientific challenges in electrochemistry due to their unprecedented structural stability that enables a harsh working environment. HEAs are a new materials class that provides single-phase stabilizations via entropic effects by mixing different species and benefits from the synergistic properties of each constituent. Moreover, HEAs are allured for catalytic applications from their increased ability to combine elements to tune the catalytic properties by regulating elements contributing to catalytic activity, selectivity, and stability.

The TELEGRAM project aims to demonstrate a complete green ammonia carbon-neutral cycle where the ammonia synthesis and its use as fuel in an ammonia fuel cell are examined. This study presents the electrocatalytic and material properties of CoCrMnNiFe for electrochemical ammonia synthesis at standard temperature and pressure.

Thin films of the HEA were prepared by magnetron sputtering. Ammonia production from nitrogen gas was examined in alkaline electrolytes having different concentrations of KOH to investigate the K⁺ ion effect on the synthesis of ammonia. The results showed that it is possible to obtain ammonia with an ammonia production rate of 10⁻¹⁰ mol cm⁻² s⁻¹ or by up to 20% Faradic efficiency at room temperature.

Keywords

ammonia synthesis, high entropy alloys, electrocatalysis

P2.94

Influence of the thickness of ionomer films on the transport behaviors in catalyst layer of PEMFC

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Abstract

Comprehension of oxygen, proton, and water transport properties in the catalyst layer is significant to improve the performance of proton exchange membrane fuel cells. The hydration level and thickness of the catalyst layer are different from the ionomer membrane. Therefore, it is obvious to demonstrate the transport phenomenon of molecules in low hydration levels at various thicknesses of ionomer films. In this study, the nanostructure of ionomer films at different thicknesses of ionomer films and their influence on the transport properties are investigated using the molecular dynamics simulation method. Our investigation improves that the development of a water channel corresponding to water volume accelerates with an increase of the thickness of ionomer films despite containing the same water ratio. Contrariwise, the distribution of free volume is reduced with increasing the thickness of ionomer films. Through these volume analyses, it is confirmed that the transport properties of water and vehicular transport of proton enhance with increasing water volume. However, the permeability of oxygen which is associated with solubility and diffusivity is affected by the free volume and has a trade-off relationship with the properties of water. Finally, it is noteworthy that the hopping transport of protons decreases with the increasing thickness of ionomer films due to the nanostructure of the water phase derived from the strong interaction with Pt particles.

Acknowledgments

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Keywords

molecular dynamics, transport property, catalyst layer, ionomer film

P2.95

Fluorescence detection of perfluoroalkyl carboxylic acids with a guanidine-functionalized benzoxadiazole dye integrated into core-shell particles

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Abstract

Perfluorocarboxylic acids (PFCAs) are a family of compounds that consist of a fully perfluorinated carbon backbone and a carboxylic acid moiety. PFCAs have been classified as substances of very high concern by REACH regulations due to their persistence in the environment, non-biodegradability and toxicological effects. Thus, there is significant interest in detecting PFCAs in ground, waste, surface and drinking water. Fluorescence detection is a portable, easy-to-operate and cost-effective alternative, enabling the onsite detection of these analytes e.g., with miniaturized fluidic sensors.

Here, a guanidine benzoxadiazole (BD) dye covalently attached to a polymerizable methacrylate unit was developed for the integration of the dye into polymers and on surfaces. The response behavior of the dye toward PFCAs was assessed in monophasic (EtOAc) and biphasic (EtOAc-H₂O) solvent systems, the biphasic system being advantageous for the extraction of the hydrophobic organic acids from the aqueous phase.

The BD dye was integrated into sensory silica core-polymer shell particles for the sensing of PFCAs directly in aqueous media. Submicron SiO₂ particles were functionalized with 3-(trimethoxysilyl)propyl methacrylate followed by radical polymerization with the BD dye and ethylene glycol dimethacrylate. TEM images showed a homogeneous polymer shell with a thickness of 75±2 nm.

By incorporating the BD dye into core-shell particles, lower limits of detection (1.52 µM for perfluorooctanoic acid, PFOA) were achieved if compared to the use of the neat BD dye in a biphasic assay (17.3 µM for PFOA), and excellent discrimination against inorganic acids thanks to the hydrophobic polymer shell. The particle sensory platform has proven to be an alternative for the sensing of PFCAs directly in water.

Keywords

PFOA, Core-shell particles, Polymer nanolayers, Fluorescence detection

P2.96

Interpreting the carbon 1s spectrum in X-ray photoelectron spectroscopy (XPS)

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Abstract

The carbon 1s spectrum is the most widely fitted and analyzed narrow scan in X-ray photoelectron spectroscopy (XPS), with a near ubiquitous application to all materials that have been exposed to the atmosphere. Indeed, various forms of carbon may be present on any surface of interest, including adventitious carbon, oxidized carbon, and graphitic carbon. Accordingly, it is critical to use appropriate protocols when interpreting C 1s narrow scans, especially because so much of the XPS peak fitting in the literature is incorrect. This poster will focus on how to appropriately fit the C 1s spectrum, highlighting specific challenges such as overfitting and fitting sp_2 carbon samples, such as reduced graphene oxide. Additionally, this poster will include an overarching guide as to how to approach peak fitting with specific considerations to unique materials such as crystalline diamond. Examples of correct and incorrect peak fitting will be provided. Overall, this presentation will provide an overview of the rules, principles, and considerations for appropriately analyzing the C 1s spectra. It will also provide a list of common errors made in fitting C 1s spectra and considerations to make during fitting.

Keywords

x-ray photoelectron spectroscopy, carbon, reduced graphene oxide, reproducibility

P2.97

Laterally ordered quantum dot arrays on virtual nanostructured Si substrates

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Abstract

Laterally ordered III-V semiconductor quantum dot (QD) arrays with high uniformity, purity and brightness, produced through a scalable and reproducible process are critical requirements for the fabrication of a variety of quantum functional devices, such as spin qubits and single photon sources. Moreover, having a low-cost and high throughput fabrication process is necessary to meet the requirements of mass production of QD-based quantum devices.

We have studied by using AFM, C-AFM, HR-SEM and PL spectroscopy the strain-induced growth of laterally ordered arrays of InAs quantum dots along the orthogonal $\langle 110 \rangle$ directions of nanostructured Si(001) templates by molecular beam epitaxy (MBE). Our results show that up to a nominal thickness of ~ 120 ML, InAs two-dimensional nucleation at 490°C takes place preferentially on the (110) vertical facets. Above this critical thickness we observed the preferred nucleation of InAs three-dimensional islands along the $\langle 110 \rangle$ -oriented edges of the template grid and, to a lesser extent, on the (001) facets at the bottom of the rectangular trenches. In addition, InAs/GaAs quantum dot heterostructures were grown under similar conditions on virtual nanostructured Si (001) substrates for photoluminescence spectroscopy (PL) studies. In these samples, a pseudomorphic 1,8 nm-thick GaAs buffer layer was deposited prior to the growth of 1,2 nm (2 ML) InAs, which was subsequently covered with a 10 nm-thick GaAs capping layer to provide the necessary optical confinement. A great improvement in quantum dot size uniformity and ordering was observed by introducing the ultra-thin GaAs buffer layer. The low-temperature PL spectra of the as-grown samples exhibit a strong peak corresponding to the TO-phonon assisted exciton emission of the Si substrate at 1,10 eV and a narrow InAs-related emission peak at 1,01 eV (FWHM=2,6 meV). Annealing of the samples at the growth temperature for 15 min resulted in a slight narrowing and blueshift of the InAs emission peak.

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Keywords

Quantum dot arrays, InAs, Nanostructured Silicon