

BOOK OF ABSTRACTS

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CONTENTS

Keynote Speakers	1
Invited Speakers	6
Oral Presentations	23
T01: Photovoltaics, photocatalysis and photochemistry	23
T02: 2D materials	25
T03: Composite materials	33
T04: Environmental, health, economic and legislative aspects of nanotechnology ...	36
T05: Novel synthesis methods and applications of nanomaterials	42
Poster Presentations	65
T01: Photovoltaics, photocatalysis and photochemistry	65
T02: 2D materials	72
T03: Composite materials	82
T04: Environmental, health, economic and legislative aspects of nanotechnology ...	87
T05: Novel synthesis methods and applications of nanomaterials	90

Keynote Speakers

The versatility of mesoscopic solar cells

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In our work on solid-state dye-sensitized solar cells (ssDSSC) we have recently shown that copper phenanthroline complexes can act as an efficient hole transporting material. We prepared ssDSCs with a novel organic dye WS-72 and $[\text{Cu}(\text{tmbpy})_2]^{2+/+}$ as redox system and achieved record power conversion efficiencies for ssDSCs of 11.7%. Our best DSC efficiency of 13.1% for a liquid Cu-complex electrolyte is achieved by the discovery that the PEDOT based counter electrode can be directly contacted with the dye/ TiO_2 photoelectrode. Thus, there is no space between the two electrodes minimizing diffusion limitations and fill factors up to 0.8 is achieved.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 22% with a mixed composition of iodide/bromide and organic and inorganic cations. With the use of SnO_2 compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20%. Through the compositional engineering larger perovskite grains grown in a monolithic manner are observed and reproducibility and device stability are improved. With regards to lifetime testing, we have shown a promising stability at 85 °C for 500 h under full solar illumination and maximum power point tracking (95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests.

Semiconductor quantum dot architectures for designing next generation photovoltaics

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Semiconductor nanoparticles are excellent building blocks for designing light harvesting assemblies. The first report on the size effect of photosensitization was published by Gerischer and Luebke.¹ This seminal paper had a significant impact on the progress of quantum dot solar cells research in the following years.² Of particular interest are the metal chalcogenide (CdS, CdSe) and metal halide perovskite (CsPbX₃) quantum dots (QDs) which are very effective as photosensitizers.³ The ability to tune the optical and electronic properties by changing the size and composition remains an attractive feature of these semiconductor materials. We have now employed these semiconductor nanostructures to study electron transfer in mesoscopic TiO₂ films. The electron transfer from excited QDs to TiO₂ is an ultrafast process occurring with a rate constant of 10¹⁰-10¹¹ s⁻¹. On the other hand the hole transfer to a redox couple or a hole transport material such as CuSCN is two to three orders of magnitude slower and remains a major limiting factor in dictating the overall efficiency in quantum dot solar cells. Photoelectrochemical and transient absorption studies that provide mechanistic and kinetic details of electron and hole transfer at the semiconductor interface will be discussed. Various interfacial charge transfer processes that limit the power conversion efficiency and strategies to overcome these limitations in solar cells will be presented.

Acknowledgment

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Benign-by-design preparation of nanomaterials for catalysis and energy production

Rafael Luque

The design of benign and environmentally sound methodologies has been the driving force of scientists in recent years. Attractive and innovative protocols that nowadays are even part of industrial ventures including biomass-derived porous carbonaceous materials as well as a range of designer nanomaterials for catalytic applications and energy conversion/storage have been recently developed in our group in recent years.

In this lecture, we aim to provide an overview of recent efforts from our group in leading the future of global scientists from chemical engineers to (bio)chemists, environmentalists and materials scientists in the search for benign-by-design approaches for nanomaterials preparation.

Organometallic hydrogels as metal nanoparticle foundry for sensing and catalysis

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Organometallic, redox responsive hydrogels have the ability to function as a versatile and facile synthetic “factory” to obtain, metal nanoparticles (NP) by direct reduction from their salts. Metal reduction can occur in a controlled way, in a one-step process and without the need of using external reducing and stabilizing agents, in the hydrogels swollen by aqueous solutions of the corresponding salts. We use polyionic derivatives of poly(ferrocenylsilanes) (PFS) with either positively, or negatively charged side groups in simple (redox) and dual (redox and temperature) responsive hydrogel forms [1]. Due to the presence of ferrocene in the main chain PFSs exhibit redox active behavior and have the ability to reduce metallic cations. Owing to the presence of the charged side groups in the hydrogel network, the PFS polymer can simultaneously function as a stabilizing agent. Depending on the reduction potential of the metallic cations with respect to ferrocene in PFS, a range of metals including Au, Ag, Pt, Pd, Rh and Ir can directly be reduced to form metallic NPs [2].

Free-standing hydrogels [2], surface anchored thin films [3], [4], as well as colloid particle dispersions [5] will be discussed. The free standing gels will provide information about the NP formation and stabilization, while electrode-anchored thin films and microparticles will offer size control. First, applications in electrocatalysis will be pursued [4]. To this end we shall employ thin hydrogel films covalently immobilized at electrode surfaces [4]. The gels will be loaded with catalytically active metallic NPs and the electrocatalytic activity will be addressed. As a model system we shall consider electrocatalytic oxidation of ethanol [4]. Finally, we discuss a simple and efficient method for the synthesis of stable and redox responsive AuNPs using organometallic polyelectrolytes in aqueous solutions of HAuCl₄ [5]. In the redox reaction, positively or negatively charged poly(ferrocenylsilanes) (PFS+/PFS-) serve as reducing agents, and also as stabilizing polymers. Due to their unique tunable electrostatic and electrosteric protection, AuNPs coated with PFS-, (PFS+)-AuNPs, possess high redox sensitivity, with reversible, repetitive, sustainable color switching between the assembled (purple color) and disassembled (red color) states as evidenced by UV-Vis absorption and TEM measurements. Feasibility studies indicate that the particles described can be applied as a colorimetric probe for the detection of redox molecules in a controlled and facile manner.

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Invited Speakers

Pristine & modified fullerenes in perovskite solar cells

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Keywords: Fullerenes, Perovskite Solar Cells

In the present communication we will focus on the use of fullerenes and fullerenes derivatives in Perovskite-based Solar Cells.

In our research group we have dedicated a great effort on the preparation and study of novel fullerene derivatives for their incorporation in perovskite solar devices. Thus, we have reported for the first time the use of pristine C₇₀ as ETL in PSCs and the utilization of fullerenes and derivatives as additives in PSCs.

Very recently we have described the incorporation of a Fullerene derivative as HTM (FU7) in PSCs, and also the concept of “fullerene sandwich” perovskite devices (Figure 1).

In this invited talk, we will discuss on these topics, highlighting the potential of the use of fullerene chemistry in order to prepare highly efficient and stable in PSCs.

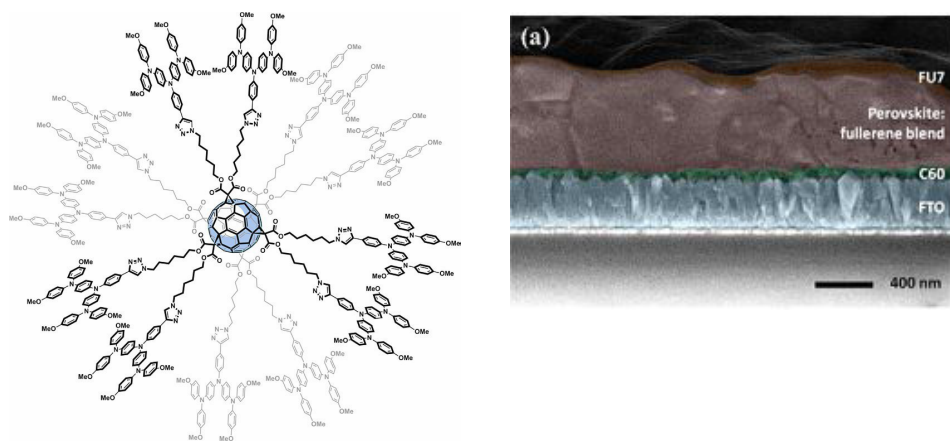


Figure 1: Left) Chemical structure of novel [60]fullerene hexakis adduct FU7. Right) Cross-section FE-SEM image of a “fullerene sandwich” perovskite device with FTO/C₆₀/pvsk:C₆₀/FU7/Au architecture.

Acknowledgments

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Near-field probing at nanostructures with <1 nm sensitivity

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Keywords: nanostructures, plasmonics, nanooptics, near-fields

Plasmonic enhancement of optical near-fields at nanostructures ensures the nanoscale localization of the energy of light. Although this phenomenon allowed pioneering applications in spectroscopy, photovoltaics and sensorics, the measurement of the maximum achievable nanoplasmonic field enhancement for a particular sample is still a challenge. Here, we present a method for nanoplasmonic near-field measurement with the help of photoemitted electrons induced by femtosecond laser pulses.

The method is experimentally demonstrated on different model systems involving nanoparticles exhibiting localized plasmons and thin films with propagating surface plasmons. As a first step, ultrashort laser pulses excite propagating or localized plasmons, of which plasmonic near fields induce photoemission of electrons into vacuum surrounding the sample. Photoelectron spectra are measured with a time-of-flight spectrometer [1,2], see Fig. 1 (a). Since the highest photoelectron energies originate from nanometric rescattering of the electrons from the metal surface, nanoscale near-fields can be measured by analyzing the cutoffs (highest electron energies) of the electron spectra (see Fig. 1 and [3]).

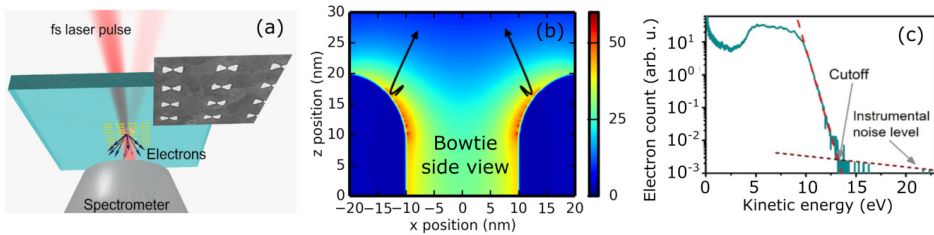


Fig. 1. (a) Scheme of the experimental setup for nanoplasmonic near-field measurement with photoelectrons (black arrows). The femtosecond laser pulse and the entrance to the time-of-flight electron spectrometer are indicated. (b) Field distribution map of the bowtie structure with black arrows indicating the trajectories of rescattered electrons. These electrons gain the highest kinetic energy, therefore they form the spectral cutoff. (c) Photoelectron spectrum with the spectral cutoff point indicated from which field enhancement is extracted.

This way, field enhancement values between 21 and 51 for 4 different samples (supporting localized and/or propagating plasmons) were *measured within <1 nm distance* from the plasmonic surface. These data are in very good agreement with the results of accurate finite-difference time-domain (FDTD) simulation of the given nanoplasmonic system. The demonstrated method, combined with more sophisticated electron imaging techniques can be extended for full characterization of nanoplasmonic near-fields promising nanometer lateral resolution. These results establish ultrafast plasmonic photoelectrons as versatile probes for nanoplasmonic near-fields enabling time-resolved studies, as well.

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Wetting and functionalisation of graphite and 2D materials

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There is much current interest in the applications of 2D materials in the context of energy storage. Another topical area is the transport of liquids and gases within the “nano-capillaries” that can be created with such materials, with particular interest in filtration and other separation-based applications. In this talk, we will discuss our recent work on the wetting of graphitic surfaces: it is clear that near “frictionless” interactions occur at the graphite-water interface [1]. We also describe methods to functionalise graphite surfaces, with covalent organic bonds and with metals/metal oxides, during the electrochemical exfoliation of graphite to graphene [2-4]. Applications of these materials in energy conversion/storage will be discussed. Finally, we will discuss the functionalisation of few-layer MoS₂ materials, and the use of such membranes for de-salination of water [5].

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Perovskite solar cells: From lab-scale to industrial manufacturing

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Keywords: perovskite solar cells, scaling up, Roll-to-Roll, industrial manufacturing, non-hazardous solvents, modules, interconnection

Research progress in the hybrid perovskite solar cells has increased enormously over the last years, making perovskites very promising candidates for future PV technologies. Perovskite solar cells use abundant and low-cost starting materials, providing economic advantages for large-scale implementation. A transition from the laboratory-scale fabrication to industrial manufacturing requires: scaling up the dimension of the devices; manufacturing of the modules; and development of deposition methods alternative to spin coating using non-hazardous solvents. All developed processes and materials should be industrially compatible and facilitate high power conversion efficiency of the manufactured devices.

The latest developments in sheet-to-sheet (S2S) and roll-to-roll (R2R) slot die coating manufacturing will be discussed along with other related technologies required for industrial-scale methods. Using optimized S2S manufacturing technologies, perovskite PV modules of 144 cm² with 13.8% stabilized efficiency on aperture area (14.5% on the active area) were demonstrated [1]. At the same time, by developing the R2R slot die deposition processes, a series of flexible modules was manufactured. The modules with an aperture area of 10.5 cm² demonstrate a stabilized PCE of 12.2% (13.5% on the active area), the active area efficiency is equal to the efficiency of the small single devices made in the same process. Moreover, the modules with an aperture area of 160 cm² exhibit a stabilized PCE of 10.1 % (11.0% on the active area) [2]. In addition, the latest achievements allow reaching a stabilized PCE of up to 16% for the devices with three R2R slot die coated layers, a development of large area modules with the same device stack is ongoing. The deposition of all layers in the R2R processes are performed using non-hazardous solvents compatible with industrial manufacturing.

In addition to the development of opaque flexible modules, large area semi-transparent modules were demonstrated. The modules show transparency of up to 50% for the entire visible range, making the modules suitable for windows application. The PCE losses in the semi-transparent modules, compare to the opaque ones, are proportional to the level of transparency. The obtained results can be considered as an important milestone towards industrial manufacturing of perovskite photovoltaics and their future commercialization.

Acknowledgments

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Nanohybrids of nanostructured amphiphilic polymer conetworks and gels: From nanocatalysis to antibacterial materials

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Amphiphilic conetworks (APCNs) [1-14] consisting of covalently bonded otherwise immiscible hydrophilic and hydrophobic polymer chains belong to a new class of rapidly emerging nanostructured materials. The structure and morphology of APCNs are shown in Figure 1.

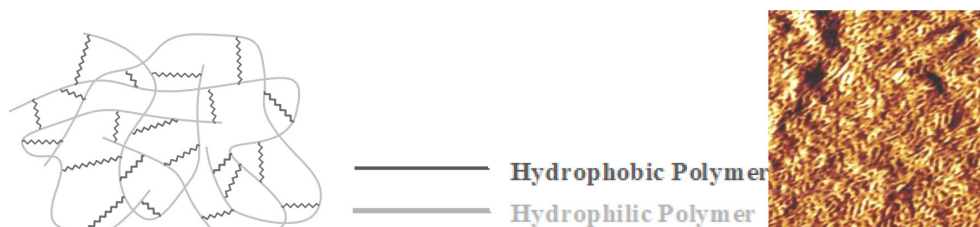


Figure 1. Schematic structure of an amphiphilic conetwork (APCN) and an AFM image of the bicontinuous nanophasic morphology (image size: 250x250 nm).

Due to the strong chemical bonds between the immiscible polymer chains, unique bicontinuous (cocontinuous) nanophase separated morphology exists in APCNs in a broad composition window. This is the basis for the preparation of various specialty new intelligent (responsive) gels and organic-inorganic nanohybrids by applying one of the nanophases as nanoreactor. The resulting novel materials have a variety of high added-value potential applications from nanocatalysis and photonics to biomaterials etc.

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Does degradation of perovskite photovoltaics require perovskite decomposition?

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I will review our experimental results on degradation of perovskite photovoltaic materials [1–3] and devices [4–7] and discuss underlying degradation mechanisms with and without nonreversible photochemical decomposition of metal halide perovskites.

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Transparent conductive films using grid-type microstructures

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Transparent conductive films (TCFs) used as top electrodes play a pivotal role in photovoltaics and display applications. In commercial devices, such coatings utilize mainly sputtered indium-doped tin oxide (ITO) and aluminum-doped zinc oxide (AZO) films. Apart from lacking mechanical flexibility of such coatings, indium is scarce and will be depleted within a few tens of years with the current pace of extraction and usage. Motivated by the above practical problems, efforts are made to find alternative materials and technologies that may offer better sustainability and possibly even more advantageous functional properties. Recent studies suggest that the application of thin film grid-type conductive micropatterns of metals (e.g. Cu, Ag, Au) and carbon nanomaterials (nanotubes and graphene) deposited on polymer surfaces by wet chemistry may be reasonable alternatives to ITO and AZO. In our work, we present two new related approaches. In the first, we show that self-assembled droplets of ink-jet printed reactive inks are suitable for depositing catalyst nanometals in microscopic grid patterns, on which then highly conductive copper can be plated. In the other approach, we apply area-selective plasma treatment on polymers through a shadow mask to locally improve the hydrophilicity of the surface in a grid-pattern thus facilitating localized wetting with aqueous dispersions of conductive nanomaterials (single-wall CNTs and graphene) which form conductive networks on the surface after drying.

Binary, doped and complex oxides as transport layers in halide perovskite solar cells

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We are moving towards a sustainable society powered by renewal energy where solar photovoltaics is one of the most important players. In the past few years, emerging photovoltaic (PV) technologies have observed an exponential increase in power conversion efficiencies (PCE) with halide perovskite solar cells above 22%, tandem photovoltaics reaching 26% or dye sensitized solar cells for indoor lighting at the impressive 28.9% PCE mark. Oxides in solar cells can be found as the main solar absorber responsible for photon-to-electron conversion, as interfacial layers for the transport of electron or holes, as part of the conductive metal electrodes (including transparent electrodes) and also as part of photon management. Among the many advantages is the ease of fabrication, low cost and enhanced stability that provide to the solar cell. Moreover, new-generation of oxides (e.g. doped or undoped, binary, ternary, ferroelectric, etc) are slowly breaking ground providing competitive power conversion efficiencies, enhanced transport properties or improved UVlight stability, among others. We report our most recent studies on the application of classic oxides (binary, doped, nanostructured) and complex oxide compounds (ternary, ferroelectric, etc.) as transport layers in Halide Perovskite Solar Cells. We will discuss their effect on solar cell efficiency and long-term stability of solar cell devices.

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Mimicking active sites of enzymes in Cu- and Fe-zeolites

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Cu- and Fe-zeolites are active catalysts of important chemical reactions such as decomposition of N_2O and NO in N_2 and O_2 and selective oxidation of methane to methanol and of benzene to phenol. Careful spectroscopic analysis has elucidated the active sites for the methane – to – methanol reaction. They are the μ -oxo dinuclear Cu core, $[\text{Cu-O-Cu}]^{2+}$ in Cu-zeolites and the high spin ($S=2$) mononuclear $[\text{Fe=O}]^{2+}$ core in Fe-zeolites. Their formation, spectroscopic signatures and activity will be reported and discussed. The dinuclear Cu site is located in zeolite channels and channel intersections with the following sequence of Si and Al-tetrahedra: Al-O-Si-O-Si-O-Al. These channels are typically eight-membered (8MR) and ten-membered ring (10MR) channels and channel intersections. The mononuclear Fe=O site is located in six-membered rings (6MR) with two Al tetrahedral opposite to each other. These sites show the importance of the Al distribution in the zeolitic lattice. It is a challenge in zeolite synthesis to control this Al distribution.

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Molecular design, synthesis and processing of nanomaterials for applications in solar cell and tissue engineering

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Through the molecular design, we are able to synthesize and process different nano materials to meet the requirements of properties and performance in solar cells and tissue engineering. The properties of nanomaterials are determined by the chemical structure (moiety) of the materials.[1] In the application of solar cells, we designed and synthesized donor-acceptor conducting polymers basis on the isoindigo moiety which is naturally occurred dye from plant. It is a sustainable raw material. In contrast to the most conducting polymers, these polymers are air stable and ease of synthesis in big quantity.[2] The polymers have been fabricated into flexible solar cell with the energy conversion efficiency reaching 10%. We are using polymeric additive to the perovskite solar cell, the performance of solar cell has been improved from 14% to 16% of power conversion efficiency [3]. Biomimic the structure of proteins, we have synthesized polypeptide using amino acid moiety through ring opening polymerization. The polymers containing neuron stimulate, glutamate, exhibit exceptional neurite growth behavior up to mm length long. The polymers have potential application in central nerve regeneration.[4]

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Organo-metal halide perovskite solar cells with superlattice

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Recently, organometal halide perovskite solar cells (PSCs) have received great attention. The power conversion efficiency (PCE) of PSCs have shown a dramatic increase and certified PCEs adopting mixed organic cations and halide anions have reached up to 22%. The PCE is considerably affected by photovoltaic property of each component of a PSC. Particularly, because crystal quality of materials is strongly concerned with the electronic properties such as carrier transport, investigation of detailed crystallographic information of the perovskite light absorber is essential. In this talk, we will report a microstructural observation about phase coexistence in the perovskite light absorber through transmission electron microscope (TEM) observation. Surprisingly, during the high resolution (HR) TEM observation, we found coexistence of tetragonal and cubic structures in the perovskite layer. This new finding is expected to be an important clue of the enhancement of perovskite crystal quality for highly efficient PSCs.

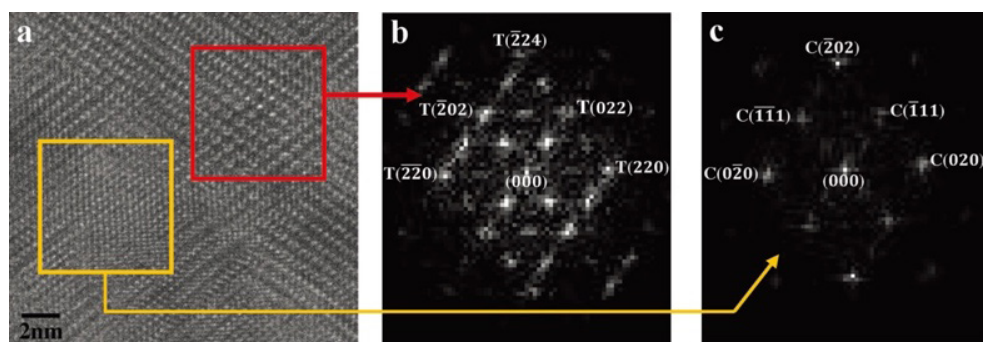


Fig. 1. HRTEM images, a) HRTEM ($\times 1000K$) image at the white rectangle of Figure 1a showing the co-existence of the tetragonal and cubic nanodomains. b) Tetragonal $T[111]$ (red rectangle) zone axis FFT. c) Cubic $C[101]$ (yellow rectangle) zone axis FFT.

Acknowledgments

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Advanced materials for state of the art energy technologies

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Keywords: hexagonal carbon nitride, transition metal dichalcogenides, hydrogen evolution reaction, oxygen reduction reaction

Green energy technologies, both generation (a.k.a. conversion) and storage, still face challenges such as low efficiency, usage of rare and expensive precious metals, environmental issues at the production or disposal, etc. In energy storage devices all of the parts have shortcoming, instability of anodes and electrolytes, limited temperature and environmental windows, energy and power density shortcoming, all these calls for new solutions built up from the very base, using new materials, structures and technologies.

In this talk, I will summarize a few results of our work to demonstrate how nanomaterials can help; I will focus on several of the recently popularized and widely researched 2-dimensional materials, graphene and materials beyond graphene as these are potent candidates for serving as a catalyst in multiple kinds of energy conversion related reactions and important building blocks of energy storage devices.

Carbon based materials, oxides and chalcogenides are three interesting and important groups of the atomically thin materials. For each of these groups, I will talk about the production, materials characterization and application aspects. The underlying scientific message of the talk: it is common in all of these examples that even in these low dimensional materials the high surface area is not sufficient, one needs to explore chemically active locations, edges and defects, to achieve competitive performance.

Interface engineering in high-performance perovskite solar cells

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Interface engineering of perovskite solar cells (PSCs) was performed and investigated at the heterojunction between titania and perovskite by self-assembling a layer of amino acids on the surface of TiO_2 . All solar cells with amino acids outperform the standard device with bare TiO_2 and the one with L-alanine gives the best photovoltaic behavior. To explore how the amino acids in the interface influences the crystallization of perovskite, the grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were carried out for the thin perovskite film on c- TiO_2 . The scattering profiles suggest that the crystallites of perovskite tend to align in the direction perpendicular to the TiO_2 surface with an ordered arrangement of Pb and I atoms parallel to the substrate, consequently reducing the barrier of transferring electrons from perovskite to TiO_2 . This finding demonstrates that the appropriate atom arrangement of perovskite crystallites in the interface is a niche for better photovoltaic performance. Additionally, by providing a comprehensive discussion on buildup and decay of open-circuit voltage (V_{oc}) under illumination and in the dark for the PSCs modified with [6,6]-phenyl- C_{61} butyric acid methyl ester (PCBM) at the TiO_2 /perovskite interface and their corresponding electrochemical impedance spectroscopies (EIS), a justified mechanism is proposed to elucidate the dynamics of interfacial species with respect to the time and frequency domains. Our results demonstrate that the retarded V_{oc} buildup and decay observed in the PSCs are related to the formation of bound charges in TiO_2 , which is essential to neutralize the oppositely charged ions accumulating at the perovskite side. Besides, inserting PCBM at TiO_2 /perovskite interface as a passivation layer can efficiently alleviate the electrode polarization as verified by the less dielectric constant measured from EIS.

Oral Presentations

T01: Photovoltaics, photocatalysis and photochemistry

Sheet-to-sheet slot die coating of mixed-cation perovskites for high efficiency non-transparent and semi-transparent cells and modules

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Hybrid-organic perovskites are proven materials for thin-film photovoltaics, with efficiencies over 23.25% at lab-scale. In order to promote the lab-scale research to fab-scale, it is essential to achieve an environmentally-friendly, affordable, and highly efficient process. Here, we report on the upscaling of sheet-to-sheet (S2S) slot-die processing of PSCs, heading towards the roll-to-roll (R2R) production. Results demonstrated that S2S upscaling from 3x3 cm² to 15x15 cm² area exhibited no loss in PCE of perovskite solar cells (PSCs). In this study, a Cs/FA/MA triple cation perovskite has been deposited as absorber layer, and metal oxide layers have been deposited as charge transport media. The highest achieved efficiency for n-i-p structure is demonstrated as 14.5% with a yield above 95% and with a geometrical fill factor over 95%, whereas for the p-i-n structure we achieved a PCE of 15% on module level using a metallic top electrode. Semitransparent devices using a transparent conductive oxide, with the same architecture yielded a PCE of 14%. We stress that using spatial ALD for coating buffer charge transport layers has significant effect to protect the underlying layers from the sputter damage during TCO coating with sputtering process. On top of that, sALD provides better coverage and stability, even alleviating the need of using multiple charge transport layers between the perovskite layer and top electrode. These results demonstrate that S2S slot die coating is a promising route for producing non-transparent perovskite solar cells and in combination with sALD, semi-transparent perovskite solar cells and modules with high efficiency and process stability is possible.

Investigation of charge carrier dynamics in metal-oxide/nanocarbon hybrid photoelectrodes

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Keywords: metal-oxide semiconductors, photoelectrochemistry, solar fuel generation, charge carrier dynamics

One of the most critical challenges of the 21st century is the shift in energy use from fossil fuels to renewable sources. Photoelectrochemical (PEC) solar energy conversion, as a potentially attractive candidate, has gained an increased momentum during the recent years. Although both water-splitting (hydrogen evolution) and carbon dioxide reduction are promising avenues, they both have substantial shortcomings to be addressed. A common virtue of these two processes is that a good photoelectrode has to concurrently fulfill many attributes to drive these reactions efficiently. One of the most important is the efficient charge carrier transport, which ensures that most of the photogenerated charge carriers can be extracted both toward the electrode/electrolyte junction and toward the back contact, without significant recombination. Numerous theoretically promising photoelectrode material showed poor PEC performance due to extensive charge carrier recombination both in the bulk and at the surface. A well-known example is α -Fe₂O₃ (hematite), in which the hole-diffusion length is only 2-4 nm.¹ One possible way to improve charge carrier transport properties is to deposit the metal-oxide on an interconnected nanocarbon network (e.g., MWCNTs or graphene). These highly conductive nanoscaffolds can effectively improve the transport of the photogenerated charge carriers, which in turn, results in an enhanced PEC performance.²

In my presentation, I am going to discuss in detail, how the charge carrier dynamics of various metal-oxide (MO) semiconductors and their nanocarbon-containing composites is affected by the composition of the nanohybrids and by the applied bias. MO/nanocarbon photoelectrodes were synthesized by a two-step method: first, the nanocarbon layer was spray-coated on the surface of the substrate electrode, and the metal-oxide component was electrodeposited on to these conductive nanoscaffolds in a subsequent step. Composition of the MO/nanocarbon ratio was precisely controlled by the deposition charge density. To investigate charge carrier dynamics on a timescale ranging from seconds to femtoseconds three different techniques were employed: (i) transient absorption spectroscopy, utilizing a fs pump-probe setup, (ii) intensity-modulated photocurrent spectroscopy, and finally (iii) fast chronoamperometry. By covering this broad timescale, it was possible to study charge carrier transport, trapping and recombination processes, which were greatly affected by both the applied potential and the presence of the nanocarbons.

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T02: 2D materials

Modelling of quasi 1D nanostructures based on 30° twisted bilayer graphene

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Keywords: bilayer graphene, carbon nanotubes, DFT

Bilayer graphene is the attractive material for future applications. It has some unique properties which distinguish from graphene monolayer. In example – existing of band gap ~100 meV in electric or magnetic fields, superconductivity if it has magic angles of twisting. Recently it was shown that different modification can results to drastically changing of electronic structure of bilayers. Creation of periodically arranged folded holes results to a wide range of conductivity from metal to semiconductor with the band gap up to 2 eV [1-3]. So combination of differently modified bilayers can be 2D fully carbon electronic device. It is important to note that some experimental works shown creation of nanostructures from graphene bilayers: folded edges [4], nanoholes with diameters $D > 1.4$ nm [5], thin nanotubes in AA stacked bilayers [6].

Here we present DFT investigation of the new class of quasi one dimensional nanomaterials based on bilayers with twist angle 30°.

Twisted 30° bilayer has the symmetry of the six order, therefore we consider 1D nanostructures along two non-equivalent periodic directions.

We choose complicate shape of edges to obtain fully sp² hybridized structure with covalent connected layers. These nanostructures can be imagine as the new type of compressed nanotubes or bilayer nanoribbons with folded edges and different oriented layers. Classification of this new nanostructures, evolution of these electronic structures depending on geometry and deformations will be presented. Comparison of this properties with properties of known structures (armchair and zig-zag nanotubes, mono- and bilayer nanoribbons) will be presented also.

All calculations were made on supecomputer centres of MSU and RAS.

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Step-by-step computational investigation 2D materials formation process on substrates

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Synthesis of graphene demonstrated the possibility of obtaining fundamentally new materials: ultrathin films with atomic thickness with unique physical properties. If at the first stages of 2D films were obtained by mechanical exfoliation from the crystals having layered structure (for example, graphene, h-BN, MoS₂, etc.), then in the future two-dimensional materials with structure and properties having no analogues in 3D, such as silicene (two-dimensional silicon), borophene (monolayer of boron atoms), etc., were synthesized.

Currently, there is a very limited set of methods for simulation of the formation process of nanostructures. These methods can only partially describe the formation of nanostructures, for example, the method of molecular dynamics (MD) at finite temperatures and manual search of a finite number of static combinations of possible intermediate structures. All these methods have significant limitations in simulation and obtaining the final result.

Necessary conditions for obtaining the desired material in the growth process is the correctness definition of the main parameters: the type and composition of the substrate, the external conditions (temperature and pressure), the definition of the necessary parameters of the cells of the substrate and the desired material, as well as their symmetry.

Here we presented an effective method for simulation of two-dimensional materials formation with one and several layers thickness on substrates of different composition based on the software package USPEX (Universal Structure Predictor: Evolutionary Xtallography). New expanded modules of the USPEX software complex allow to simulate the formation of low-dimensional nanostructures and predict the crystal structure of low-dimensional materials with random composition consisting of more than 2 types of atoms on different substrates depending on external parameters (temperature, pressure).

Applied extended USPEX modulus simulation of the formation of 2D nanostructures with atomic layers thickness (including graphene, h-BN) and several layers thickness of a given composition (including NaCl, LiCl) on various substrates (including Cu, Ni, Ag, graphene, diamond) were carried out. Obtained results has an excellent agreement with available experimental data.

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Graphene oxide membranes as swellable structures

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Keywords: graphite oxide, graphene oxide, intercalation, exfoliation, polar solvents

Graphene oxide (GO) is the most prominent functionalized graphene derivative. A remarkable property of GO is easy hydration/solvation by vapours or liquids, which results in expansion of interlayer distance. Intercalation of GO powders using liquid solvents is rather rapid and typically saturates within minutes, in contrast with intercalation by vapours which, depending on the vapour pressure, may take hours to achieve equilibrium state. The present structural study shows that the GO membranes exhibit unique hydration/ solvation properties, not found in precursor graphite oxide powders (Figure 1). In particular, both GO membranes and graphite oxides are hydrated very similarly in pure water, but insertion of ethanol and methanol into the GO membrane structure is hindered, being limited to one monolayer while in the graphite oxide powders up to 3–4 layers of these solvents can be inserted. The tunable solvation/layer expansion properties of graphene-based membranes are relevant for various materials science applications including particle synthesis in the interlayers or membrane separation of solutes by size exclusion mechanisms.

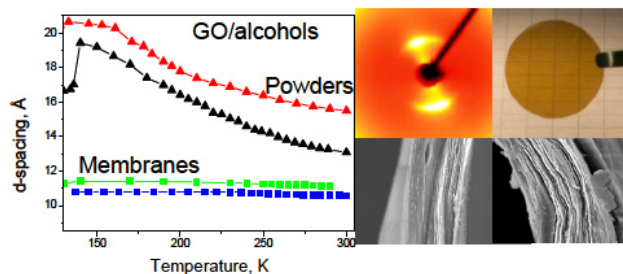


Figure 1. Left: The temperature-dependence of the basal spacings of powdered vs membrane samples of GO immersed in alcohols. Right: X-ray diffraction image and usual and electron microscopic appearance of a GO membrane.

Acknowledgments

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Few layers graphite fragments: thermal properties investigation

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Keywords: few layers grafite fragments (FLGF), nitrogen doping, heats of combustion

Few layers graphite fragments seem to be very perspective carbon nanomaterials due to their ability to be easily functionalized. Their defectiveness and a great amount of edge carbon atoms lead to a bigger rank of heterosubstitution and oxidation in comparison with MWCNTs [1]. It became necessary to find a universal parameter that is applicable for the characterization of FLGFs and draw some parallels among them. Because of the sensitivity of the heat of combustion value to structure features, defectiveness and heteroatoms quantity in material it appeared to be a desirable one.

All samples were obtained with pyrolysis of various organic precursors and their mixtures in quartz reactor. The formation of FLGFs' unique structure took place on magnesium oxide template [2]. With varying synthesis' parameters six series of samples were obtained. The major factors that were varied in each of them: nitrogen or oxigen content, defectiveness, specific surface area and thickness.

The defectiveness of the materials and edge atoms content were analyzed by means of Raman spectroscopy. General nitrogen content and nitrogen different types presence were investigated with elemental analysis and XPS respectively. Specific surface area and pore size distribution were studied with low temperature nitrogen adsorption method. Simultaneous thermal analysis was chosen for heats of combustion measurements due to some limitations of bomb calorimetry application. Heats of combustion were calculated from corresponded exothermic effects areas.

It was found that the heats of combustion of non-doped FLGFs' monotonously increase in absolute value with enlarging of graphene layers quantity and could be explained as contribution of steaking energy between the layers. For nitrogen-doped FLGF's with quite similar values of specific surface area it was found that the heats of combustion decrease with the increase of nitrogen content. But in case of different specific surface area of N-FLGFs some competitive dependences could be found out.

Acknowledgments

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Photoelectrochemical investigation of two-dimensional semiconductors applying a microdroplet-electrochemical cell

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Keywords: 2D semiconductors, exfoliation, photoelectrochemistry

The first studied members of two-dimensional (2D) semiconductors, the transition metal dichalcogenides, have become one of the most well-studied members of “2D materials family” beyond graphene, because of their high chemical stability and good electrocatalytic properties^{1–2}. The key challenges in utilizing graphene³ and the other 2D materials² in energy-related applications are (i) to precisely control their chemical reactivity and (ii) to obtain solid knowledge of their photoelectrochemical (PEC) behavior. For example, the structure- and morphology-dependent surface electron transfer kinetics, double layer capacitance, and light-harvesting efficiency have to be better understood^{1–3}. Considering the reactivity dependence of 2D semiconductors on their spatial and structural properties (i.e. the basal/edge planes, the number of layers, and the defect density), a microscopy-based approach is highly required to investigate their electrochemical and PEC properties.

Firstly, I will start my presentation showing our recently developed custom-designed microscale PEC setup. This approach consists of four main parts: i) the sample area is selected with a microscope; ii) the microdroplet is deposited (Figure 1A); iii) the electrochemistry is controlled/monitored by a potentiostat–galvanostat; and iv) the illumination is provided with a fiber-optic light source with controlled wavelength and intensity (Figure 1B). The deposited 10–50 µm sized microdroplet acts as an electrochemical cell on the chosen sample area of the 2D crystal (contacted as working electrode), which will be illuminated by a spot size at 25–50 µm in diameter. Then, I introduce the micromechanically produced 2D materials (MoSe₂, WSe₂, MoWSe₂) with different structural properties, for example, the number of layers and the defect density. Finally, I present our results on the effects of the structural properties of mechanically exfoliated flakes for their PEC performance (Figure 1C). Our studies demonstrate the first experimental results in this direction.

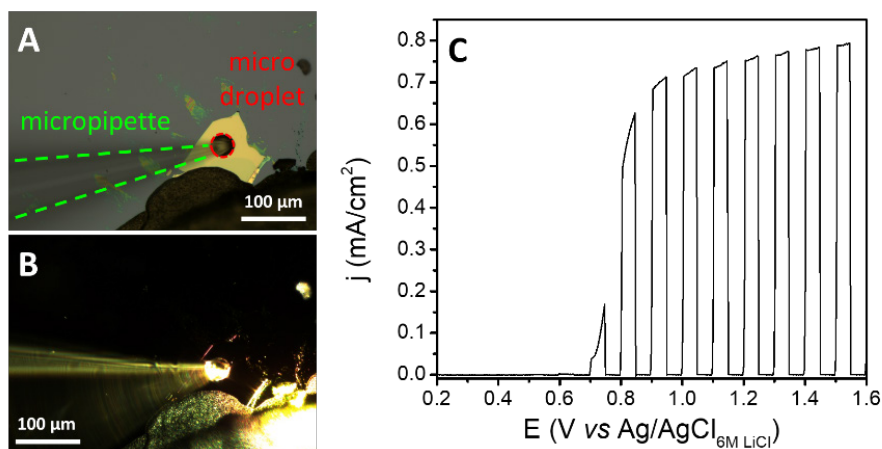


Figure 1. Optical micrographs of a droplet deposited on the surface of a single crystal bulk MoSe₂ flake, without (A) and with (B) white light illumination. The dashed lines indicate the micropipette (green) and microdroplet/flake interface (red). C: Linear sweep photovoltammograms recorded for the illuminated droplet on micrographs A–B, in 6 mol dm⁻³ LiCl aqueous solution.

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Ambient oxidation of 2D MoS₂ basal plane imaged at single-atom level

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The ambient oxidation of two-dimensional (2D) molybdenum disulfide (MoS₂) crystals is generally viewed as being restricted to under-coordinated sites at edges and grain boundaries, while the defect-free basal plane remains environmentally inert [1]. Here we provide atomic level insights into the ambient oxidation reaction of MoS₂ monolayers by scanning tunneling microscopy measurements and DFT calculations [2,3]. We found that oxygen gradually incorporates into the basal plane of 2D MoS₂ crystals through a substitutional oxidation reaction, by replacing individual sulfur atoms, while fully preserving the original crystal lattice. The resulting 2D MoS_{2-x}O_x solid solution crystals are characterized by catalytically active basal planes, where substitutional sites can be identified as active reaction centers, increasing the catalytic activity for electrochemical H₂ evolution reaction. The observed oxidation process enables the chemical modification of single atomic sites of 2D crystals opening new routes towards their efficient defect engineering.

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T03: Composite materials

New tungsten borides, their stability and outstanding mechanical properties

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Operation of many of the industrial application is not possible without using superhard materials. Nowadays it is highly likely to search for new cheap and effective materials which can substitute traditional materials in many field of science and technology. Traditionally material can be called as superhard if its Vickers hardness is higher than 40 GPa [1–3].

Here we predict new tungsten and molybdenum borides, some of which are promising hard materials that are expected to be thermodynamically stable in a wide range of conditions. We computed the composition-temperature phase diagram, which shows the stability ranges of all predicted phases. New boron-rich compound WB_5 is predicted to be superhard with Vickers hardness of 45 GPa and at the same time it possesses high fracture toughness of $\sim 4 \text{ MPa} \cdot \text{m}^{0.5}$ [4]. Newly predicted tungsten and molybdenum boride (WB_5 and MoB_5) are found to be thermodynamically stable in a wide range of temperatures at ambient pressure. Temperature dependences of the mechanical properties of WB_5 were studied using quasi-harmonic and anharmonic approximations. Our results suggest that WB_5 and MoB_5 remains a high-performance material even at very high temperatures.

The work was supported by Russian Science Foundation (Grant No. 17-73-20038).

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Immobilization of natural or artificial biocatalysts on polyelectrolyte functionalized inorganic nanoparticles

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Keywords: antioxidant enzyme, metal complex, titania, layered double hydroxide, bionanocomposite

Antioxidant enzymes are the primary defence systems against reactive oxygen species (ROS). Enzyme supplementation is a promising way to deal with increased ROS concentrations, however, their high sensitivities to the environmental conditions make this impossible either in parenteral or oral administration. Therefore, various nanoparticle systems are being developed to deliver enzymes in immobilized forms. The present results were obtained in systems containing nanoparticles (titania nanosheets (TNS) and layered double hydroxides (LDH)) and enzymes (superoxide dismutase (SOD) and horseradish peroxidase (HRP)) or enzyme mimicking metal complexes.

The TNS and LDH were prepared hydrothermally first and functionalized with polyelectrolytes to improve their colloidal stability and to promote immobilization of the biocatalysts. The aggregation processes were suppressed by adsorbing a saturated layer of the polyelectrolytes on the particles. The structural integrity of the SOD and HRP enzymes was kept during immobilization and the enzymatic activities were very similar to the bare enzymes and they possessed the advantages of the heterogeneous catalysts. Besides, an enzyme mimicking metal complex, namely copper(II)-histamine ($\text{Cu}(\text{Hsm})_2$) was immobilized on poly(4-vinylpyridine-co-methyl methacrylate) (PVPMAA) functionalized LDH platelets (Figure 1). As revealed in electron paramagnetic resonance spectroscopy measurements, the complex was attached to the copolymer via coordinative bonds between the copper(II) ions and the nitrogen of the pyridine groups. The obtained hybrid material showed good SOD-like activity. More importantly, its superoxide radical scavenging ability was kept even at higher temperatures, where the native SOD lost its function after a few minutes. Summarily, the above discussed antioxidant systems showed great activity in ROS decomposition and formed highly stable dispersions. They are promising candidates in applications either in biomedical treatment or industrial processes, wherever the aim is to reduce ROS concentration.

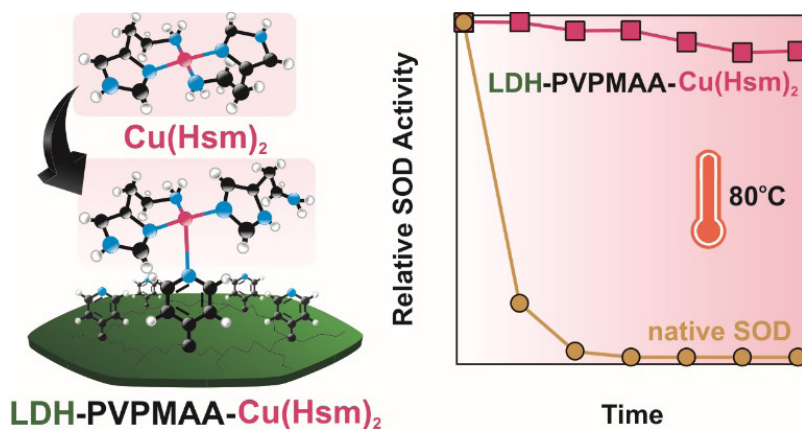


Figure 1. Scheme of immobilization of $\text{Cu}(\text{Hsm})_2$ complex on copolymer functionalized LDH particles (left) and superoxide radical scavenging activity of the bare SOD and its mimic at elevated temperature (right).

Acknowledgments

The authors are grateful for the support of the Hungarian Academy of Sciences (Lendület, 96130).

T04: Environmental, health, economic and legislative aspects of nanotechnology

Unravelling the hazards of metal nanoparticles to *Eisenia andrei* and *Eisenia fetida* immune cells: an *in vitro* approach

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Keywords: silver and gold nanoparticles, toxicity, earthworms, coelomocytes, gene expression

Metal nanoparticles (NPs) are among the most widely used commercial and biomedical nano-products. Until now, little is known about the immunological consequences of NP exposure. Among terrestrial invertebrates, earthworms are “keystone” sentinel organism to estimate the health of the soil ecosystem.

We hypothesized that earthworm immune cells (so called coelomocytes) as macrophage-like cells, are highly susceptible to the toxicity of NPs. We applied *in vitro* 10 nm silver (Ag) NP and gold (Au) NP exposures to *Eisenia andrei* and *E. fetida* coelomocytes with different concentrations (1.25 µg - 40 µg) and incubation intervals (4 and 24 hours). Our aim was to analyse the effects of NPs on molecular and cellular levels in earthworm coelomocytes.

First, we characterized the physical features of NPs by spectrophotometry and dynamic light scattering. Cell viability was ascertained with flow cytometry measurements (7-Amino-actinomycin D and mitochondrial membrane-potential assessment). Cell death mechanisms were investigated with Caspase-3 fluorescent substrate and TUNEL assay. Direct estimation of DNA damage was determined with Comet assay. Q-PCR measurements were executed to evaluate the gene expression of a pattern recognition receptor (TLR), stress molecules (Cu/Zn SOD, metallothionein) and antimicrobial factors (lysenin, lumbricin, lumbricin-related peptide) in various time periods (2, 12, 24 hours).

We observed concentration dependent cell death in both species (*E. andrei* LC10: 1.64 µg, LC50: 16.7 µg and LC90: 27.53 µg; *E. fetida* LC10: 1.18 µg, LC50: 5.24 µg and LC90: 23.25 µg) exposed to AgNP. AuNP treatments yielded no significant alterations in the viability compared to control cells in either species. AgNP caused elevated level of Caspase-3 and TUNEL positive cells as well as induced the depolarization of mitochondrial membrane and DNA damage. At the cellular level *E. fetida* coelomocytes showed higher sensitivity compared to *E. andrei* coelomocytes. Q-PCR analyses revealed that both NPs treatment led to changed mRNA expression patterns in investigated genes. Generally, the expression patterns were rather similar in both species. Treatment of AgNP for 24 hours evoked significantly up-regulated expression level of TLR, Cu/Zn-SOD, lumbricin, and lumbricin-related

peptide genes. In both species decreased lysenin mRNA expression was observed by AgNP treatment. In contrast, metallothionein expression showed significantly augmented mRNA expression only for *E. fetida*. AuNP treatment had no major influence on the expression patterns of the investigated genes.

Comparison of different metal NPs revealed some remarkable differences in their mechanisms of action. Based on our results AgNP are more toxic to coelomocytes than AuNP. Furthermore, *E. fetida* coelomocytes are more sensitive to NPs treatments compared to the coelomocytes of *E. andrei*.

Acknowledgements

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Biosynthesized silver and gold nanoparticles are potent antimycotics against opportunistic pathogenic yeasts and dermatophytes

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Keywords: silver nanoparticles, biological synthesis, dermatophytes, opportunistic pathogenic yeasts, antifungal activity, toxicity

Epidemiologic observations indicate that the number of systemic fungal infections has increased significantly during the past decades, however in human mycosis, mainly cutaneous infections predominate, generating major public health concerns and providing much of the impetus for current attempts to develop novel and efficient agents against cutaneous mycosis causing species. Innovative, environmentally benign and economic nanotechnology-based approaches have recently emerged utilizing principally biological sources to produce nano-sized structures with unique antimicrobial properties.

In line with this, our aim was to generate silver nanoparticles (AgNPs) and gold nanoparticles (AuNPs) by biological synthesis and to study the effect of the obtained nanoparticles on cutaneous mycosis causing fungi and on human keratinocytes. Cell-free extract of the red yeast *Phaffia rhodozyma* proved to be suitable for nanoparticle preparation and the generated AgNPs and AuNPs were characterized by transmission electron microscopy, dynamic light scattering, ultraviolet–visible spectroscopy and X-ray powder diffraction. Moreover, a complex biological screening was carried out to determine the toxicity of silver and gold nanoparticles to human keratinocyte cells as well as against various fungal species with a special emphasis on antifungal efficiency against dermatophytes.

The results indicate that the yeast mediated green synthesis was successful in both cases, the assynthesized silver and gold nanoparticles were phase pure, well crystalline with a face-centered cubic structure and have the characteristic peak which can be attributed to surface plasmon resonance. Furthermore, screening of their biological activities confirmed that the silver nanoparticles exhibited good antimicrobial activity against all examined microbial species whereas the gold nanoparticles were toxic only to *Cryptococcus neoformans*. None of the silver or the gold nanoparticles were toxic to human cells in the applied concentration range. Our results emphasize the therapeutic potential of such biosynthesized nanoparticles, since their biocompatibility to skin cells and their outstanding antifungal performance can be exploited for topical treatment and prophylaxis of superficial cutaneous mycosis.

Acknowledgments

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Designing hierarchically structured fibrous materials exhibiting superhydrophobic properties using nano-scale features

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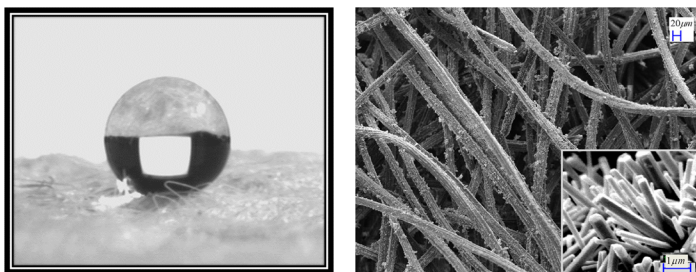
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Keywords: Nonwovens, superhydrophobicity, nanorods, mathematical modelling

Superhydrophobicity has gained tremendous attention in the recent years. Researchers have successfully mimicked many naturally occurring superhydrophobic surfaces such as wings of butterfly, water strider legs or plant leaves. This inspiring notion of nature has stimulated researchers in various disciplines to mimick these surfaces by designing and tailoring the nanometre scale topography on micrometre-scale surfaces. However, materials such as nonwoven mats are quite irregular and heterogeneous in nature as they essentially consists of fibres orientated randomly or directionally which are not regularly spaced and distributed in stochastic or non-stochastic manner. This heterogeneous nature of nonwovens can significantly enhance their hydrophobic characteristics due to the protuberances caused by the defined regions covered by overlapping fibres¹. Thus, the main objective of the research work is to propose a step-wise approach based upon theoretical modelling and extensive experiments to modulate the surface wettability of superhydrophobic nonwoven materials with hierarchical roughness and low surface energy². Since, these nonwoven materials have constituent fibres with secondary features in the form of nanorods. It is anticipated that these nonwoven materials can be potentially used as 'self-cleaning' materials. In general, this behaviour of nonwoven mat is significantly important for many practical applications such as water repellent textiles, filtration, separation, protective clothing, tissue engineering, drug delivery, anti-static coatings, anticorrosion protection, etc.

Figures



Nonwoven mat decorated with ZnO nanorods
Water drop on hierarchically structured nonwoven mat

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Miniaturized sensor fabrication using AerosolJet Technology for biological and chemical detection

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Keywords: AerosolJet, biosensor, chemical sensor, biomolecule printing

Interest in high-density biomolecule printing directly in microfluidic cells, in particular proteins is in the forefront of current life science applications. Moreover protein microarrays have been developed as low-cost, time-saving alternative to traditional proteomics methods such as chromatography or gel electrophoresis and have shown double-digit market growth in the last few years. Likewise there is a high interest for printing chemical sensors inside reactors and lab wares. For example printing technique is used for accurate monitoring of cell culture environments or to control the atmosphere in food package.

An additive manufacturing tool will be presented: Aerosol jet technology to print biomolecules and chemical sensors. Aerosol jet printing has emerged as a mature method to print temperature and solvent sensitive biomaterials in a non-contact, mask-less manner. These properties are particularly important to integrate sensors directly in fluidic and to print sensitive biomolecules like antibodies or DNA. Up to now this technology is mostly used in electronics and solar cell industries. In this presentation, the integration of this additive manufacturing tool into the fabrication of protein microarrays and the miniaturization of sol-gel based chemical sensors will be presented.

The feasibility of functional antibodies printing will be demonstrated. High printing resolution combined with excellent homogeneity will be highlighted. The antibodies' reactivity will be confirmed by running immunoassays with the printed microarrays and quantified using a fluorescence array scanner.

Finally, performances of an oxygen sensor printed by of the oxygen sensitive dye incorporated into a solgel matrix will be presented.

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The heat of sorption of organic pollutants on the surface of pristine and N-doped carbon nanomaterials

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Keywords: carbon nanotubes, N-doped materials, organic vapours, heat of sorption

There are plenty of organic pollutants that are dangerous for aqueous and aerial environment. The traditional method of separation is mechanical filtration. Due to their porosity and tunable physicochemical characteristics carbon nanomaterials with various types of structure have several advantages as filtrating materials [1]. The possibility of introducing heteroatoms in graphene layers can improve the selectivity of adsorption of desirable pollutants [2].

The aim of this work was to determine the heat of sorption of acetone, ethylacetate and toluene on carbon nanomaterials surface as well as nitrogen-doped ones. Two types of carbon structures were selected: carbon nanotubes (CNT) and carbon nanoflakes (CNF). Carbon nanomaterials were obtained by pyrolysis of benzene (pristine CNT and CNF) and acetonitrile (N- CNT and N- CNF). Adsorption properties of nitrogen-doped carbon nanostructured powders as well as pellets, obtained by spark plasma sintering method, respective to ethanol, acetonitrile, heptane, benzene, water and 1-methylimidazole were studied by DVS Advantage instrument (SMS, UK). Experimental heats of sorption of all the solvents on carbon nanomaterials' surfaces were calculated according to: $-R \frac{\ln\left(\frac{p_2}{p_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}}$,

after measurements at 20 and 30 °C. Organic vapour sorption measurements are compared to liquid nitrogen sorption data. Thermal analysis was performed to determine amorphous carbon and noncombustible residue content. Composition and chemical state of N atoms of CNTs and CNF surface was identified by XPS method.

The specific surface area calculated from organic vapour sorption appears to be in agreement with that calculated from liquid nitrogen adsorption measurements for all tested materials. The values of the heat of acetone adsorption were found to be –34.1, –33.5, –35.8 kJ/mol on CNT, N-CNT, N-CNF respectively although on pristine CNF –38.4 kJ/mol. It was found that heat of adsorption values are affected by effective molecular areas of adsorbate, their dipole moments as well as carbon nanomaterials morphology. CNF have the largest surface area and are presumably the best adsorbents for polar substances. CNTs are the most suitable for toluene adsorption among all studied materials.

Acknowledgments

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T05: Novel synthesis methods and applications of nanomaterials

The H₂–D₂ exchange reaction catalyzed by gold nanoparticles supported on γ -Al₂O₃: Effect of the particle size on the reaction rate

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Keywords: hydrogen, gold nanoparticle, isotopic exchange, size effect

The hydrogen isotope exchange reactions arouse special interest, as they are used in nuclear isotope enrichment and thermonuclear fusion techniques. Catalytic properties towards reactions involving hydrogen are inherent in transition d-metals in which the presence of vacant d-orbitals gives rise to the ability to adsorb hydrogen. Metals that complete the transition metal series, Ni, Pd, and Pt, are known to exhibit especially high activities towards H₂-D₂ exchange and towards hydrogenation of organic compounds. However, the neighboring metals, Cu, Ag, and Au, which have completely filled d-shells, are absolutely inactive at low temperature. Meanwhile, as we have noted, when taken in the nano-sized state, chemically inert gold does show activity towards hydrogen isotope exchange.

The H₂-D₂ exchange can be considered as a model for investigation of organic reactions that involve hydrogen and are catalyzed by gold nanoparticles, as the isotope exchange is always preceded by atomization of the hydrogen molecule. Previously, H₂ + D₂ isotope exchange catalyzed by systems containing gold nanoparticles has almost not been studied.

The aim of this work was to systematically investigate the effect of the size of gold nanoparticles on their catalytic activity towards hydrogen isotope exchange and to elucidate the relationship between the “size effect” and structural inhomogeneity of the particle surface. For this purpose, gold particles with a wide size variation from 0.7 nm and up to 40 nm were synthesized. The study demonstrated with certainty that increasing the size of γ -Al₂O₃-supported particles induces a 750-800-fold decrease in the specific catalytic activity at 77 K. The method of preparation of gold particles does not affect the catalytic properties. The nanoparticle catalytic activity was found to be correlated with the presence of low-coordinated gold atoms on their surface (Fig. 1).

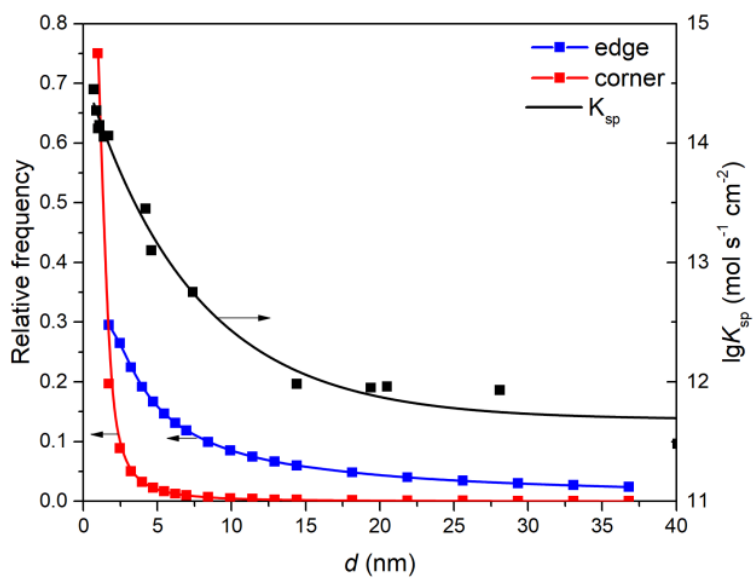


Fig. 1. Size dependences of the specific catalytic activity and relative frequency of edge/corner surface atoms of gold nanoparticles in isotopic exchange reaction at 77 K.

Synthesis of nitrogen-doped graphene nanoflakes and their applications in supercapacitors

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Keywords: carbon nanomaterials, ionic liquids, inorganic electrolytes, supercapacitors

Electrochemical double layer capacitors (EDLs), or supercapacitors, are considered as promising energy storage devices due to the reversible non-faradaic charge storage. For practical application the most important parameters of EDLs are power and energy densities. Charge storage capacity of EDLs may be enhanced by tuning both electrolyte and carbon-based electrodes. Doping of carbon material with heteroatoms, such as nitrogen and boron, is an effective way to modify its chemical and electronic properties. The substitution of carbon atoms in graphene layer with nitrogen or boron makes this material n- or p-type semiconductor. Moreover such modification not only improves surface wettability of carbon material but also introduces pseudocapacitance that is especially important for its electrochemical applications. This work focuses on the synthesis of N-doped graphene nanoflakes (GNFs) with high nitrogen doping level of 10.6 at. % and their application as an electrode material in EDLs with an organic electrolyte. N-GNFs were synthesized at 800°C by chemical vapor deposition technique using acetonitrile as a precursor and MgO as a mesoporous template. To optimize porosity of the material the synthesis time of 0.25, 0.5, 1, 1.5 hours was used, which resulted in the N-GNFs specific surface area of 1000, 820, 580 and 440 m²/g, correspondingly. XPS showed the presence of pyridone, pyridine, pyrrole and graphitic nitrogen species in the synthesized materials.

The operating voltage of EDLs with an aqueous electrolyte is limited by the narrow electrochemical stability window of water. In contrast, organic electrolytes allows to increase operating voltage up to more than 2.7 V resulting in high power density and specific energy of EDLs. In this work imidazolium-based ionic liquids (ILs) such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM⁺TFSI⁻) and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM⁺TFSI⁻) were used as electrolytes with high electrochemical windows [1]. The specific and molar conductivities of ILs were measured in acetonitrile solution, that was used to decrease viscosity and, consequently, to improve charge transfer and mobility of electrolyte ions. The highest specific conductivity of such acetonitrile-based solutions depended on the cation size and was equal to 5.82 S/m for EMIM⁺TFSI⁻ and 4.87 S/m for BMIM⁺TFSI⁻. Resulted capacitance of EDLs with N-doped GNF-based electrodes achieved up to 180 F/g while that for non-doped GNFs it didn't exceed 100 F/g. The capacitances of N-GNF based EDLs was found to be proportional to the specific surface area of N-GNFs.

Acknowledgments

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Rapid and selective detection of dopamine on molecularly imprinted polypyrrole/carbon nanotube polymer electrodes

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Keywords: molecular imprinting, dopamine, neurotransmitters, microelectrodes, selectivity

Several neurodegenerative syndromes in the central nervous system are mainly caused by the depletion of dopamine. Monitoring such low concentrations under *in vivo* conditions is not straightforward, but electrochemical methods, such as differential techniques, fast scan cyclic voltammetry and chronoamperometry are attractive candidates. However, selectivity plays a vital role, because biological samples contain a lot of electroactive components and there is only a slight difference between the oxidation potential of these molecules. Designing a sensor however, which is selective for one compound is challenging, because the signal can come from multiple electroactive components. Furthermore, some of them could even poison the electrode surface, making the detection impossible.

In this work, we have synthesized a highly sensitive and selective electrochemical sensing material for dopamine, using the molecularly imprinted polymer skeleton of overoxidized polypyrrole and carbon nanotubes. Galvanostatic polymerization of pyrrole was carried out in aqueous suspension of carbon nanotube, pyrrole and dopamine. The dopamine acted as a template, around which the polymer was formed as a cast-like shell. Extraction of the template leaves sites in the polymer with specific shape and functional groups responsive only to the original template molecule. The extraction was in KOH solution by potentiodynamic cycling, where the simultaneous electrochemical oxidation of polypyrrole also occurred. The differential pulse voltammetric measurements were performed in phosphate buffer solution with the pH adjusted to the physiological value. The molecularly imprinted layer can detect dopamine at very low concentrations (the limit of detection is 50 nM) even in multicomponent samples, based on its oxidation peak current. The prepared sensor showed high sensitivity for dopamine (greater than 90 $\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$) in the presence of ascorbic acid.

Acknowledgement

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3D frameworks of sintered cobalt modified carbon nanotubes with variable magnetic, electrical and catalytic properties

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Keywords: spark plasma sintering, carbon nanotubes, cobalt particles, magnetic properties, CO hydrogenation, 3D framework

Unique conductive, structural, optical and chemical properties of carbon nanotubes (CNTs) open the way for their applications in many fields of science and chemical technology as catalytic supports, electrode materials, adsorbents, additives, electronics etc. However, low bulk density and the powdery nature of CNTs hamper their utilization in many areas, which makes their compaction important for practical use. Spark plasma sintering (SPS) is a promising and widely used technique for the production of CNT contained materials. At the same time, CNTs are usually used as an additive to metals or ceramics and only few papers are dedicated to the sintering of materials contained CNTs as a base component.

This work is devoted to the synthesis of a new type of 3D-material, in which carbon encapsulated cobalt nanoparticles are embedded into the dense framework of CNTs (Fig.1a,b). For this purpose, oxidized CNTs decorated by 4–6 nm Co oxide nanoparticles were sintered by SPS at different temperature (Ts) and cobalt content at 30 MPa. Obtained composites were carefully characterized by electron microscopy, XPS, XRD, Raman spectroscopy and vibrational magnetometry. We found that the Co particle size, electrical conductivity and ferromagnetic properties of composites can be tuned in a wide range by varying Ts (Fig.1c). Under SPS the defects in CNTs are transformed into graphitic shells that stabilize cobalt metal crystallites, which enhances the conductivity of composite (up to 12500 Sm/m) [1].

Catalytic properties of the sintered samples contained 10 wt.% of Co were studied in CO hydrogenation. It was found that cobalt nanoparticles covered with carbon shell are active in this process without pre-activation and that hydrocarbons up to C₁₂ can be synthesized at 20–50% CO conversion. Promising properties of produced materials for the magnetic separation were also demonstrated.

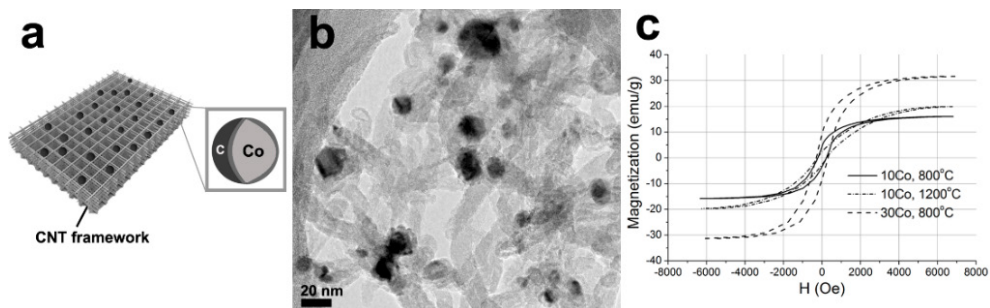


Fig.1. The scheme of the composite structure (a); TEM image of the Co/CNT sample sintered at 800°C (b); Hysteresis loops for the samples with different cobalt content and different T_s (c).

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Selective electrochemical hydrogen evolution on protected catalyst surfaces

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Keywords: hydrogen evolution reaction, cathode selectivity, water splitting

Technologies converting between electrical and chemical energy typically suffer from losses due to low selectivity. Photochemical or electrochemical hydrogen production is a common example, where solution processes or side reactions, such as the cathodic reduction of oxidatively formed products lowers the process efficiency. Accordingly, research fields from electrochemical or photocatalytic water splitting to the industrial electrochemical production of sodium chlorate share a need for electrochemically active and selective surfaces.^[1]

Here we present how different coatings formed on model catalyst surfaces induce selective hydrogen evolution (HER) in the presence of different solution species. Most importantly, the HER efficiency is studied in the presence of dissolved oxygen and hypochlorite. The HER kinetics is not significantly affected by the coatings, suggesting that the electrochemical reaction proceeds on the buried catalyst/coating interface. Showing various examples, we highlight that these coatings are passive elements, responsible for the selective transport of different solution species to the electrode surface, while supporting ample amount of water for the HER. Such nanomembrane coated catalysts therefore represent a very attractive avenue for the development of selective catalyst surfaces for electrochemical and photochemical water splitting^[2] and for industrial processes driven in undivided electrochemical cells.^[3]

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Silver nanoparticles stabilized by carbonate ions: oxygen effect

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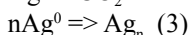
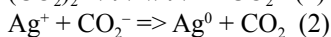
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Keywords: silver, nanoparticles, carbonate ions, hydrosol, photosynthesis, reduction

Silver nanoparticles find wide use as effective antimicrobial agents in consumer and industrial applications. A widely used process for the preparation of silver nanoparticles is reduction of silver ions in solutions, first of all, in water. New method for obtaining of pure silver nanoparticles stabilized by carbonate ions, and the effect of oxygen on their properties are discussed. For this, the reduction of Ag^+ ions was done using oxalate, which reduced Ag^+ ions and was thus converted to carbonate ions. The reduction process was initiated by pulsed UV light.



Carbon dioxide is transformed in water into carbonate ions, which stabilize silver colloidal particles



As LSPR band grows, the absorption maximum gradually shifts to blue region approximately from 410 to 390 nm. The average particle size in deaerated solution is 10.3 ± 3.2 nm. The ζ -potential of the colloidal particles formed is -68.32 mV.

The reduction of Ag^+ ions by the $\text{C}_2\text{O}_4^{2-}$ ions also takes place when UV irradiation is carried out in air. The limiting absorbance corresponding to complete Ag^+ reduction is attained over a longer period. The LSPR band is much broader and lower in intensity than that recorded for the deaerated solution. As the band grows, the absorption maximum, in contrast to the deaerated solution, gradually shifts to red region approximately from 398 to 406 nm. The red shift of the absorption band of silver nanoparticles is due to the partial oxidation of the metal during its formation. Apparently, active oxygen in the form of O_2^- partially oxidizes silver nanoparticles, including in its lattice and on the surface. In this case, most likely, insoluble silver oxide Ag_2O is formed. LSPR band of silver nanoparticles "doped" with oxygen unlike the particles obtained in deaerated solutions, shifts to the red region, which is caused by a decrease in the concentration of "free" electrons in them. The average size is 21.9 ± 4.6 nm and the ζ -potential of the resulting colloidal particles in the presence of oxygen is -68.32 mV.

Sizes and distribution of silver particles in deaerated and aerated hydrosols do not change markedly with prolonged exposure after their preparation. The ζ -potential of silver particles in hydrosols remains at nearly the same level ($\zeta = -(60-70)$ mV) for first several weeks after their preparation. The hydrodynamic diameter of silver nanoparticles varies also insignificantly. The absolute value of the ζ -potential higher than 60 mV is indicative of a high stability of the silver hydrosol stabilized with carbonate ions. The aggregation of nanoparticles is

prevented by the decrease in the interfacial tension caused by the formation of electric double layer on the particle surface.

The obtained results demonstrate new silver hydrosols synthesis composed of nanoparticles with a size of 4 nm to 16 nm and 15 nm to 30 nm by UV irradiation of the solutions containing $(1-3) \times 10^{-4}$ M of Ag^+ ions and $(3-10) \times 10^{-4}$ M of oxalate ions in the absence and in the presence of air, respectively.

These hydrosols are free from compounds that are usually employed as reducing agents or stabilizing additives and also the products of their decomposition, which may be toxic towards living nature or affect functioning of living organisms. Silver hydrosol completely corresponds to the composition of natural fresh water and can be used as effective disinfectant.

Nitrogen doped nano carbons using iron based catalyst

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Keywords: red mud, carbon nano tubes, nitrogen doping, iron oxides

N doped carbon nano tubes (CNTs) show lower turn-on field but higher current density than pure carbon nanotubes. They can be used to replace platinum in polymer electrolyte membrane (PEM) fuel cells, as sensor materials and lithium ion battery electrodes [1-3]. Iron is one of the commonly used catalysts for preparation of N doped CNT using chemical vapour deposition of carbon (in the presence of NH₃ or N₂) or using CN gas phase precursors [1]. In this study, red mud, an iron containing waste from aluminium industry was used as catalyst. Nitrogen modified carbon nanotubes were prepared using different precursors; acetonitrile, pyridine were used as carbon and nitrogen source. These were mixed with other hydrocarbons (methane, benzene) and saturated in argon or nitrogen. The experiments were carried out in the temperature range 700 °C – 800 °C.

The carbon and nitrogen content varied with processing conditions. With acetonitrile, maximum C and N were obtained at 800 °C. With the addition of methane to the acetonitrile there is no nitrogen observed at higher temperatures (800 °C and 900 °C) while with the addition of benzene to the acetonitrile there is a decrease in the overall amount of carbon deposited but nitrogen content in the CNTs is observed at higher temperature. It is observed that the graphite peak is of greatest intensity in the case of acetonitrile. The iron / iron carbide content is different with different precursors with prominent iron carbide peaks in the case of the acetonitrile and methane mixture, and prominent iron peaks with acetonitrile and benzene. Raman spectroscopy showed two main peaks at 1355 and 1575 cm⁻¹ corresponding to the D band and G band and radial breathing modes (RBM) in some samples (200 to 280 cm⁻¹) which are fingerprints of single walled CNT and diameter in the range of 0.9 to 1.18 nm was estimated.

Transmission electron microscopy analysis for acetonitrile revealed a bamboo like structure; some were open ended while some had catalyst particle at the end of the tube; at lower temperature the nanotubes were more curled and the compartments were much more uniform in comparison to the nanotubes formed at higher temperatures. XPS analysis showed different binding states for the nitrogen. Based on the properties of the N-CNTs, potential applications will be discussed.

Acknowledgments

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Electrochemical reduction of CO₂ on N-doped carbon electrodes: understanding mechanism and the role of morphology

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Keywords: CO₂ reduction, N-doped carbon electrode, isotopic labeling, effect of morphology

Electrochemical CO₂ reduction is a promising way to produce fuels and chemicals in a controllable process, while using a greenhouse gas as a starting material. *Nitrogen-doped carbons* (N-Cs) are emerging catalysts in this field, because of their high activity, tunable structure, yet significantly lower cost compared to precious metals¹. Most studies on N-C catalysts concentrated on investigating the role of different types of N-atoms on the CO₂ reduction activity and selectivity. Many questions, however, remain open regarding the reduction mechanism and the effect of catalyst morphology on the electrocatalytic performance.

In the first part of my presentation I am going to show, how ¹³C isotopic labeling experiments can be employed to furnish mechanistic insights into the reduction process. The reduction of CO₂ was performed on a polymer-derived N-doped carbon electrode in solutions of selectively labeled initial carbon sources (¹³CO₂ and H¹³CO₃⁻) under *non isotopic equilibrium* conditions. The isotopic composition of the CO product was monitored by GC-MS. These studies were combined with electrolysis experiments conducted in electrolytes with different pH values. We found bicarbonate anions as the predominant source of the CO reduction product².

In the second part, I am going to show our systematic studies to elucidate the effect of *porosity* on the CO₂ reduction performance of metal-free N-C-catalysts. We used template synthesis to modulate the morphology of the carbon catalyst. By changing solely the pore structure we could tune the overall activity and also the selectivity of the reduction process.

Better understanding of the above-listed parameters is very important in designing new electrodes, such as the metal-nitrogen doped carbons³, and new electrochemical cell configurations to scale up this technology.

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Au-Sn bimetallic electrocatalysts for electrochemical CO₂ reduction

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Keywords: Au-Sn Bimetallic Nanoparticles, electroreduction, CO₂, formate

The electrochemical reduction of carbon dioxide (CO₂), forming valuable products has attracted a great attention as a smooth step towards a sustainable development.¹⁻² This appealing approach has a dual benefit of mitigating CO₂ emission and providing a pathway for renewable energy storage and utilization, and thus enable us to reduce the dependence on traditional fossil fuel.³ Bimetallic electrocatalysts offer unique flexibility to tailor the activity and selectivity in electrochemical CO₂ reduction. Here, we report on the composition-dependent electrocatalytic behavior of Au–Sn bimetallic nanoparticles towards the reduction of CO₂. A series of bimetallic electrocatalysts with different Au–Sn intermetallic phases were obtained via tin incorporation into the gold lattice through gradual diffusion. The reaction products of CO₂ reduction were carbon monoxide and formic acid from the reduction reaction and hydrogen from water-splitting. Notably, the phase composition of the bimetallic catalysts had a massive influence on both the activity and the product distribution. Importantly, the electroreduction products always differed from that obtained for the respective physical mixture of gold and tin nanoparticles with similar ratio. Under optimal conditions, two high-value products formed with reasonable current density: formic acid in the liquid phase and syngas in the gas phase. Selective isotopic labeling studies demonstrated that the formation of carbon monoxide and formate is due to the reduction of the aqueous CO₂ supplied primarily through fast equilibrium with the bicarbonate in the close vicinity of the electrode, rather than the dissolved CO₂ in the bulk solution. The achieved control over the product distribution on Au-Sn nanoparticles demonstrated the promise of nanostructured alloys to be employed as efficient catalysts in the electroreduction of CO₂.

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Solution combustion synthesis of Cu–Cu₂O–CuO composites

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Keywords: copper oxide-based photoelectrodes, PEC carbon-dioxide reduction, SCS synthesis

One of the greatest challenges of this century is to consume environmentally friendly energy instead of the conventional non-renewable ones. The largest renewable energy source is the sunlight, which might be harnessed using the knowledge gained in the field of photoelectrochemistry in the past 35 years.

Photoelectrodes can utilize solar energy in several ways: solar energy is either converted into electricity or stored in the form of chemical energy. This strategy includes photoelectrochemical (PEC) hydrogen evolution and PEC carbon dioxide reduction into useful fuels.

There are multiple requirements that a photoelectrode must comply with: (I) it has to be stable, (II) insoluble in the test medium, (III) resistant to photocorrosion; but in the meantime, (IV) it is expected to have a broad optical excitation regime, and (V) to show good charge separation-, and transfer behavior, etc. One single material, however, cannot meet all these criteria. For this reason, composite materials are often considered, which contain several different components. These components are selected according to their individual task, for example, being a co-catalyst, or responsible for photoabsorption, etc. Design and synthesis of an effective composite photoelectrode material is a major enterprise – hence, it has become one of the main research projects in the field of photoelectrochemistry.

In this study, we investigated the synthesis of mixed copper oxide composites (which contain copper(II) oxide, copper(I) oxide and elementary copper) with solution combustion synthesis (SCS). We know from our previous works^[1] and the literature^[2] that the copper(I) oxide-based photoelectrodes can be utilized in carbon dioxide (photo)electroreduction. There are also examples that combine copper(I) oxide with copper(II) oxide resulting in an increased efficiency and/or selectivity^[2]. In this study, we applied the SCS method because it is a simple, cost-effective tool for the rapid screening of different materials. We investigated the effect of the fuel to oxidizer (F/O) ratio in the synthesis, and with X-ray diffractometry, we measured and calculated the composition (CuO:Cu₂O:Cu ratio) of the samples. We also developed one improved technique to prepare mixed copper oxide composite photoelectrodes and used in PEC reduction of carbon dioxide. A number of structural characterization methods and different photoelectrochemical techniques were performed. The products formed were determined by gas and liquid chromatography.

The results show that the F/O ratio strongly influenced the composition of the mixed copper oxide samples^[3]. These well controlled copper oxide composites were successfully applied as photoelectrodes in PEC reduction of carbon dioxide, too. In general, these results can be used in the rational design and synthesis of composite photoelectrodes to obtain potentially attractive candidates for PEC energy conversion schemes, such as water splitting or CO₂ reduction.

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Post doping synthesis by hydrothermal treatment and properties of N-CNT for composites, catalysis and electronics

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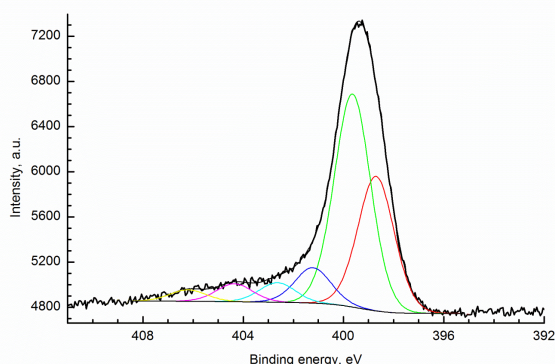
Carbon nanotubes (CNTs) have been intensively studied because of their remarkable electronic, mechanical properties and unique one-dimensional (1D) structures. Due to their nano-size features, conductivity and thermal stability, carbon nanotubes have been considered as ideal candidates for the components in multifunctional composite materials, photocatalysis, electronic nanodevices.

Up to now one of the main approaches to improve a special properties of the final materials was N-dopping of O-CNTs by other atoms. Introduction of nitrogen into the CNT structure can change electronic and chemical properties dramatically. Also such materials are applicable in industrial catalysis and electronic industry.

There are some ways to prepare N-CNTs, like chemical vapor deposition (CVD) N-containing reagents, chemical modification method or impregnation by N-containing precursors with its further decomposition. Present work deals with hydrothermal technique application for this reason.

In recent years, hydrothermal methods and supercritical fluids (SCF) have been widely utilized in science because of SCF has a low viscosity, high diffusivity, near zero surface tension, and strong solvent power for many of small molecules. The hydrothermal synthesis often is a one-step synthesis for composites and other materials.

A fluid media, water were used. As a source of nitrogen NH_3 and $(\text{NH}_3)_2\text{C}=\text{O}$ we used. The condition of one-step synthesis N-CNT was changed from 140–400°C and 0.5–48 hours. N-CNT material, obtained in hydrothermal way, have been characterized by TA, XPS and SEM. It was found optimal parameters - reaction time, temperature and agent. It was shown that the 3 hour is enough to obtain a maximum N-containing in CNT and optimal temperature is close to 180 °C, and NH_3 as a N-source is a little preferable than a urea.



Pic.1. XPS high-resolution N 1 s spectra of CNT-N with component approximation.

Flexible supercapacitors from carbonized films of electrospun lignin nanofibers

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Keywords: Supercapacitors, Carbon nanomaterials, Biomaterials, Lignin

Carbon nanomaterials that have sp² hybridized atoms are considered as excellent candidates for supercapacitor electrodes as their high specific surface area, good electrical conductivity and lightweight ensure high specific capacitances and power densities. Having bio-based carbon nanomaterials, we may add-on further benefits such as low cost and sustainable feed-stock. Here, we present a scalable synthesis route of carbon nanofiber films derived from lignin, one of the most abundant biopolymers on the Earth and available in massive quantities as a side-product of bio-fuel production. In our process, nanofiber films are electrospun from dispersions of lignin and polyvinyl alcohol, and then carbonized at temperatures between 800 and 1400°C to form self-similar freestanding porous carbon nanofiber networks with high specific surface area. The carbonization temperature offers a good parameter to tune chemical, wetting and electrochemical properties of the fibers while leaving the general structure of the films intact. As we show, the methodology is robust and offers large-scale production of flexible supercapacitor electrodes with specific capacitances that compete with those of carbon nanotube based devices.

Modulating the surface wettability of carbon nanotubes with interface engineering aided three-dimensional (3D) nonwoven material

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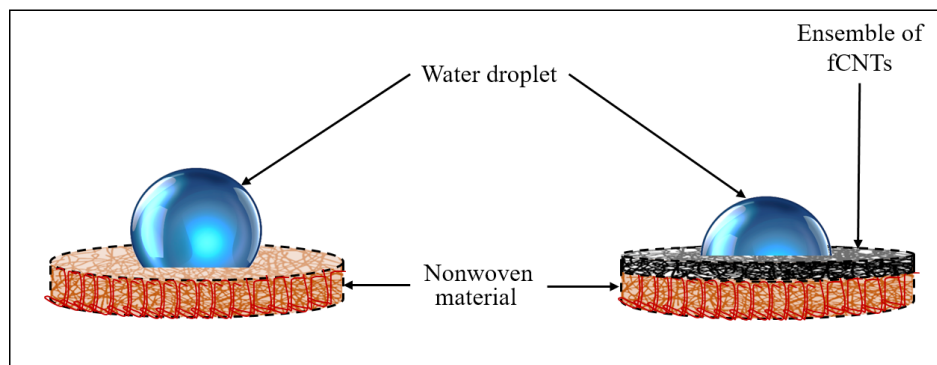
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Keywords: Carbon Nanotubes, hydrophobicity, hydrophilicity, nonwovens, mathematical modelling

Carbon nanotubes (CNTs) possess an unprecedented set of properties, which enabled these materials to pave the way for a myriad of commercial and promising applications. To diversify the portfolio of applications, it is imperative to develop a simple approach that can assist in the transition of hydrophobic to hydrophilic state of CNTs in a well-controlled manner. Herein, we report an ensemble of carboxylic functionalized CNTs decorated on the surface of three-dimensional (3D) needlepunched nonwoven material using a facile, scalable and inexpensive vacuum filtration process for tunable surface wettability. Increasing the amount of CNTs on the surface of a highly hydrophobic nonwoven material has systematically reduced the apparent equilibrium contact angle. A simple analytical model has been proposed to predict the apparent equilibrium contact angle by formulating a direct relationship with the structural parameters of CNTs and 3D nonwoven material. In the analytical model, the 3D fiber orientation distribution of nonwoven material obtained via 3D optical profiler was used as a key input parameter in predicting the apparent equilibrium contact angle of CNT decorated nonwoven materials. With the aid of analytical modeling, the structural parameters of nonwoven materials were found to play a dominant role in modulating the apparent equilibrium contact angle. However, higher magnitudes of both volume fraction of fibers and CNTs inevitably resulted in the lowest value of apparent equilibrium contact angle.

Figure



Water drop on nonwoven mat (Left) and on nonwoven mat decorated with ensemble of fCNTs

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Catalysis revolution: Nanotechnology for green future

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Keywords: Pt Nanoparticles, Controlled size, Mesoporous Oxide, Hard template – Replica Method, Heterogeneous Catalysis

Billions of dollars are investigated into information industry. Its less known, that similar budget is used for planning catalysis and industrial catalytic processes. The increasing demand for high activity and selectivity products needs new technologies and understanding of heterogeneous catalysis. The former trial-and-error method can be exchange with new techniques using in-situ methods for molecular level understanding under reaction conditions as well as controlled nanotechnology. These techniques may be exploited in CO₂ activation as well as other green methods.

In our research, mono and bimetallic nanoparticles with controlled average sizes were synthesized and anchored them on different 3D mesoporous oxide materials (SiO₂ – MCF-17, SBA-15, Co₃O₄, MnO₂, Fe₂O₃, NiO, CeO₂) prepared by the soft and hard template (replica) method. Tuning the size of the particles as well as the oxide/metal interfaces high activity and selectivity processes are favorable. NAP-XPS as well as DRIFTS techniques helped for molecular level understanding of the processes for future catalysts design.

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The financial support of the Hungarian National Research, Development and Innovation Office through the GINOP-2.3.2-15-2016-00013 project “Intelligent materials based on functional surfaces – from syntheses to applications” and the Ministry of Human Capacities through the EFOP-3.6.1-16-2016-00014 project is acknowledged.

Thermochemistry of carbon nanostructures

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Keywords: carbon nanotubes, graphene, enthalpy of combustion, enthalpy of formation, bomb calorimetry, functionalized nanotubes, graphene oxide, graphene foam

The continuous growth of the number of investigations of different types of CNMs is linked to the perspectives of their use in electronics and energy storage, catalytic industry as well as adsorbents. Numerous of works are devoted to their synthesis and investigation of physico-chemical properties, studying of correlations between characteristics, theoretical calculations and experimental search for material with the optimal parameters for certain area.

Nevertheless, only small part of research is devoted to the key parameters for all types of CNMs – their thermodynamic characteristics. To the best of our knowledge enthalpy of formation, entropy and free Gibb's energy are determined only for limited number of CNMs. Since carbon nanostructures do not possess the molecular composition as it is common for the classic substances, the question of the calculation of these characteristics till now remains open.

The correlations between structure, composition and thermodynamic parameters of different types of CNMs sometimes are contradictory, since rather limited literature data. When calculates, it is necessary to account not only temperature and pressure but also their size, possible inhomogeneity of composition, structure of particles and the presence of impurities. Present work summarizes literature data on thermodynamic properties of CNMs and their nitrogen-doped analogues reveal some experimental aspects, necessary to figure out the correlations between their structure and experimentally observed enthalpy of formation.

Original experimental results on thermochemical features of different types of carbon-based nanostructures were obtained by adiabatic bomb calorimetry and thermal analysis. It was demonstrated that the enthalpies of their formation are extremely sensitive to the structure, specific surface area, heterosubstitution as well as presence of functional groups and adsorbed species on their surface. It is shown that the $\Delta_f H_{298}^0$ values for CNTs are positive and increase with graphene layers number in their structure. After separating the contributions of surface and bulk components from this value, it was shown that second one is positive and determined by number of inner carbon layers as well as their organization. The disorder of layers and CNT defectiveness increase the enthalpy of formation. The surface component of $\Delta_f H_{298}^0$ appeared to be negative and determined by the content of adsorbed water and functional groups.

The enthalpy of formation of N-doped CMNs has non-linear correlation with nitrogen content since strongly depends on the type of nitrogen (substituted, pyrrolic and pyridine-like). Substituted nitrogen was found to be more stable and provide additional stabilization for CNM structure. The surface layers, mostly containing pyridine-like N, provoke their defectiveness, affinity to water adsorption and NOx groups formation.

The structural features and composition of CNMs under discussion were studies by HR-TEM, elemental analysis and XPS.

Acknowledgments

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Wetting and evaporation on the forests: Comparison of CNT- and ZnO-forests

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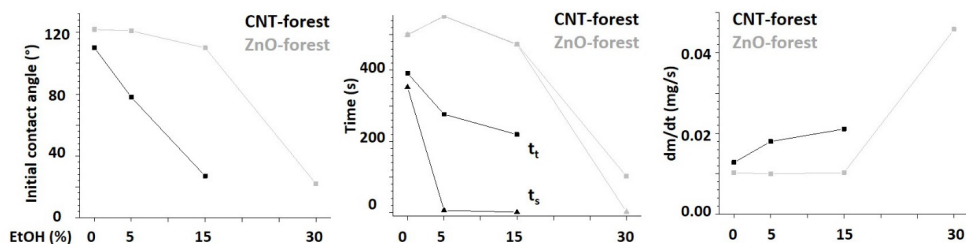
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Keywords: CNT-forest, ZnO-forest, wetting, evaporation

Recent developments in nanotechnology have highlighted the importance of the classical topics of wetting, droplet spreading and evaporation due to their pronounced effect in technological applications. Arrays of vertically aligned nanotubes and nanowires form so called forests structures, which offer unique characteristics not available with disordered states. The multifunctional carbon nanotubes (CNTs) are a typical candidate for the preparation of forest structures, but there are several other suitable materials, such as zinc oxide (ZnO). The main goal of this work was to obtain a more detailed picture of the surface properties (namely, wetting and vaporization) of the CNT- and ZnO-forests prepared by chemical vapor deposition (CVD) method and electrochemical deposition.

The evaporation of sessile droplets (e.g. water, ethanol, water-ethanol mixtures, etc.) was studied first by contact angle measurements at room temperature after that by simultaneous weight monitoring and infrared imaging at 50 °C [1-2]. There are several parameters characteristic for the evaporation process, the most important ones being the initial contact angle, the total evaporation time (t_t), time of evaporation only from the surface (t_s), evaporation rate (dm/dt), initial area of the droplet (S_d), and the wetted area at the moment of total evaporation from the surface (S_w) [1].

It was proved by using statistical methods (e.g. Pearson correlation coefficients), that the experimentally determined values are specific for the physical properties of the solvents, and they are also dependent on the quality of the solid materials, therefore, they can be used for qualitative chemical analysis via the estimation of physical properties. The results allow us to presume the possibility of this experimental setup and theoretical approach for a potential future application in the field of analytics.



Characteristic parameters for the evaporation as a function of the ethanol content in the studied ethanol-water mixtures for CNT- and ZnO-forest.

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Poster Presentations

T01: Photovoltaics, photocatalysis and photochemistry

Photoreactive hybrid nanoparticles for elimination of interfacial pollutants from water surfaces

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Keywords: polystyrene (pSt), pSt/TiO₂ and pSt/AgTiO₂ nanoparticles, composite, photocatalysis

The development of new materials with photocatalytic property has been on the focus of interest [1-4]. TiO₂ and modified TiO₂ photocatalysts are widely used in different applications like environmental and energy fields, including self-cleaning surfaces, air and water purification systems, sterilization and photoelectrochemical conversion [5].

The main goal of our present work was to synthesize organic/inorganic nanocomposites which can collect and then photodegrade the floating organic pollutants (e.g. mineral oil) on the surface of water.

The nanocomposites were synthesized using cross-linked polystyrene (pSt) nanoparticles with TiO₂ (Degussa P25) and Ag-TiO₂ photocatalyst content. Due to the hydrophobic nature of pSt matrix the composite particles shows non-wetting properties in aquas media which means that this particles can float on the surface of water and can collect the surface organic pollutants (e.g. mineral oil).

The plasmonic Ag-TiO₂ photocatalyst particles were shown photocatalytic properties under LED-light irradiation ($\lambda_{\text{max}} = 405 \text{ nm}$). The structure and morphology of the obtained TiO₂/pSt and Ag-TiO₂/pSt nanocomposites were examined by SEM and TEM measurements.

The photocatalytic activity of the prepared hybrid thin films were verified with ethanol photodegradation tests which was measured under LED light illumination ($\lambda_{\text{max}} = 405 \text{ nm}$). The photooxidation measurements were determined by gas chromatography (Shimadzu GC-14B) and the photoactivity of the reactive particles was also presented in the case of artificial surface organic pollutants.

Acknowledgments

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Enhanced p-i-n planar perovskite solar cell efficiency and stability by defect passivation with thiophene derivatives

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Surface defects of perovskite are considered as a crucial factor to determine the efficiency and stability of devices. In term of efficiency, the presence of vacancies induce trapped state in perovskite films and further deteriorate the devices performance. For stability, the vacancy sites are vulnerable to be accumulated by gas molecules. It will trap the gas molecules from environment, especially oxygen, and release electrons immediately under light illuminate. The vacancies induced electrons will react with other elements and degrade perovskite, which further affect the devices stability under light.

To overcome the issues caused by surface defects, a simple post-treatment of thiophene salt has been developed to passivate the perovskite surface defects. From the results of KPFM and Urbach energy analysis, the perovskite films with post-treatment exhibits not only less charges accumulation in grain boundaries but also lower level of electronic disorder than the films without post-treatment.

The results directly reflected on the performance of devices. The power conversion efficiency of device boosts from 15.03% to 17.18% with 2.5 mM thiopheneethyl chloride as passivating material. The 30-second measurement of current verse time plots (J-T plots) show the stable output, PCE variation within 1%, of post-treatment devices under continuous light illumination. In this study, we demonstrate that the post-treatment for as-prepared perovskite films show obviously improvement in the performance and stability of devices. It provides a feasible solution process approach to obtain high quality perovskite films without complicated process.

High efficiency perovskite solar cell fabricated by blade coating using nontoxic solvent system

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Low cost, solution processable perovskite solar cell has potential for large-scale fabrication. The blade coating is one of the coating techniques that uses less amount of material as compared with spin coating. At present, the power conversion efficiency (PCE) of perovskite solar cell has reached to 20% by blade coating. However, the device is fabricated by toxic solvent system such as dimethylformamide (DMF) in the glove box. It will be desirable to fabricate the device in air using environmental friendly solvent system for large-scale commercialized device fabrication. In this work, we successfully demonstrate the non-toxic solvent system by mixing dimethyl sulfoxide (DMSO) and γ -Butyrolactone (GBL) to deposit the perovskite film using blading coating in air. The highest PCE of 12.30% is reached for $\text{CH}_3\text{NH}_3\text{PbI}_3$ based perovskite device without post annealing.

Multi-functional electron transport layer for semi-transparent P-I-N planar perovskite solar cell

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Recently, there has been a shift in attention from improving the efficiency of perovskite solar cell to the development of semi-transparent perovskite solar cell for building-integrated photovoltaics system (BIPV) and perovskite/silicon tandem solar cell. High quality transparent electrodes emerged to be a critical issue for developing high efficiency semi-transparent perovskite solar cells. Transparent indium tin oxide (ITO) is a good top electrode material for the fabrication of device with the structure of FTO/NiOx/Perovskite/[6,6]-Phenyl-C61-butyric acid methyl ester (PCBM)/ branched polyethylenimine (PEI)/ITO due to its high transmittance, high conductivity, and high stability. However, the ITO layer is usually fabricated by plasma deposition which will damage two organic layers: electron transport layer of PCBM and work function modification layer of PEI in the device. To overcome this issue, we design and synthesize a new room temperature processable “multi-functional electron transport layer” composed of tetrabutylammonium hydroxide modified SnO₂ nanoparticles (TBAOH-SnO₂) in ethanol. This multi-functional electron transport layer can simultaneously protect the underneath layer during plasma deposition and tune the work function of ITO. High efficient and stable semi-transparent P-I-N planar perovskite solar cell was fabricated using TBAOH-SnO₂ new material. Furthermore, a robust transparent perovskite module was fabricated to demonstrate the feasibility for actual usage in renewable energy.

Morphological evaluation of hydrothermal synthesized copper oxide nanoparticles

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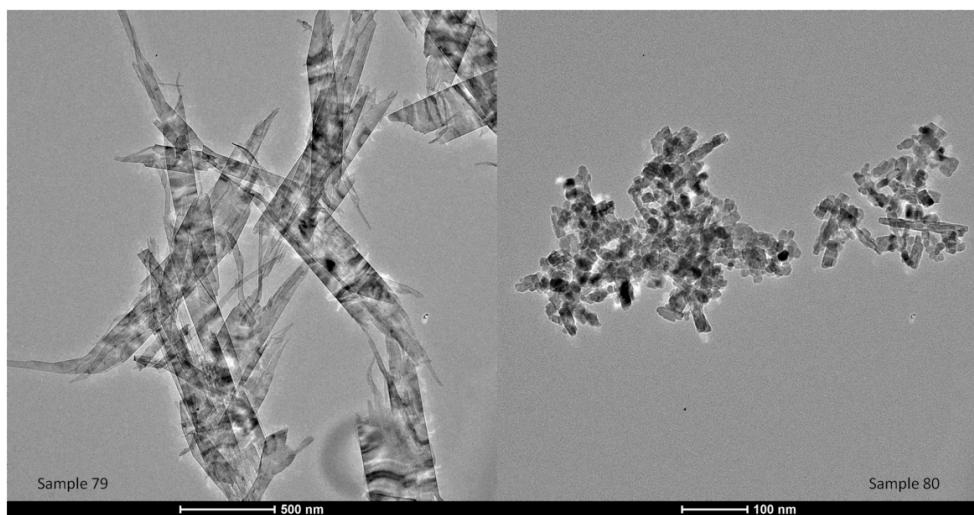
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Keywords: copper oxide, XRD, TEM

Hydrothermal synthesis of CuO nanoparticles in different morphologies by a facile and cost effective method has been experimented at room temperature and 100 °C [1]. The effect of different temperature and the effect of the mixing conditions resulted CuO nanoparticles with different shape and size, achieving rod, belt like nanoparticles.

In every experiment the precursor is used totally, the copper acetate is converted in CuO nanoparticles in very strong basic environment (pH > 12). The sample shape and size were analyzed in transmission electron microscope (TEM), the quality of the nanoparticles were determined with the help of electron diffraction images and x-ray diffraction (XRD) techniques. The observed d values are similar on the XRD patterns whit the CuO standard d values (JCPDS 48-1548)[2].



The difference in shape and size of CuO nanoparticles synthesized on room temperature (sample 79) and 100 °C (sample 80).

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Improve surface property of hot-casting perovskite film by incorporating hole transport polymer additive

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Hot casting is a promising method to fabricate perovskite thin film, due to its simple and ultrafast processing features. Besides, by hot casting methods, the moisture in the atmosphere shows minor influence on device performance, which is the main restriction for other deposition methods. However, owing to the short grain growth time of hot casting method, its film morphology is relatively rough and the defect density in grain boundary is high. Addressing this issue is the crucial factor towards high efficiency and good stability. Here in our work, by adding polvinylcarbazole(PVK) into the perovskite precursor solution, we can improve the film formation property, smooth the surface of perovskite film, diminish the amount of grain boundary and passivation surface trap state. In addition, PVK can be use as hole transporting material. Therefore, incorporation of PVK can also help to extract hole from perovskite layer. A 14.91% stabilized power conversion efficiency can be achieved when adding 1wt% PVK into perovskite, which is higher than 13.96% of pristine one. This research provides a simple way to fabricate perovskite in ambient air, providing potential guidelines for commercial large area manufacturing.

T02: 2D materials

Electrocatalytic activity of Co₄N/nitrogen-doped graphene composites in the oxygen reduction reaction

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Keywords: fuel cell, nitrogen-doped graphene, cobalt-nitride, oxygen reduction reaction

The replacement of fossil fuels is one of the most important challenges of our time. Fuel cells offer sustainable, modern alternative, however standard catalysts contain high-cost heavy metals. To replace the most common catalysts in the oxygen reduction reaction, non-noble metal catalyst appeared in the last few decades, such as transition metal-oxides, -nitrides, or metal free catalysts like nitrogen-doped graphene.

In this work we demonstrated a simple method where cobalt-nitride and nitrogen-doped graphene were synthesized simultaneously to achieve a commercially viable alternative for conventional catalysts. The as-produced catalysts possess excellent electrocatalytic activity, furthermore they proved to be promising candidates in anion exchange membrane fuel cells. Our samples were produced from lyophilized graphene-oxide and cobalt(II)-acetate in ammonia flow at high temperature. The particle size and morphology of the graphite sheets and cobalt-nitride particles were assessed by transmission electron microscopy (TEM). The structural properties of the composite were identified using x-ray diffractometry (XRD). The electrochemical and catalytic properties of the catalysts were measured as a function of cobalt-nitride content in a three-electrode cell in oxygen saturated potassium-hydroxide solution by a rotating disk electrode (RDE) in different rotation rates.

The catalyst containing 10 w/w% cobalt proved to be the most effective as its electron transfer number was the closest to 4 out of our synthesized samples. In conclusion we found the optimal concentrations of cobalt-nitride and nitrogen-doped graphene for a promising non-noble metal catalyst that can be used in oxygen reduction reaction.

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Tracking the oxidation of black phosphorus in the few-layers regime

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Keywords: Phosphorene, anisotropy, black phosphorus, *in situ* Raman, oxidation

Exfoliated black phosphorus (BP) is a promising material for optoelectronics with exponential growing interest around the world. BP is an intrinsic p type semiconductor with a thickness-dependent electronic band gap varying between 0.3 eV and 2.0 eV, but it suffers of prompt oxidation compared with other 2D materials. Oxidation threatens BP applications as the electronic structure can be completely modified by the oxygen incorporation, therefore the importance of the better understanding of the oxidation processes. Theoretical studies have predicted the presence of different types of oxides and we have demonstrated their relative thermal stability by studying the crystal structure, vibrational properties and thermogravimetric analysis. For the first time in literature, *In situ* Raman spectroscopy shows the lattice deformation by the interstitial oxygen bonding at higher temperatures. Mass increase, endothermic and exothermic processes were detected with TGA and DSC measurements at the same range of temperature. The process is reversible which enables opportunities for molecular switches using few-layers black phosphorus. The better understanding of black phosphorus oxidation unlocks the possibility to passivation with native oxide layers and the engineering of the electronic modifications can improve the feasibility of certain applications.

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Gas sensing properties of exfoliated black phosphorus nanocomposites

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Keywords: Phosphorene, heterojunctions, nickel oxide, gas sensor, 2D materials

Recent studies have demonstrated the advantages of 2D materials for environmental applications and has called the attention around the world due to its monoelemental composition, biocompatibility and electronic and optical properties. Different target molecules have been investigated with black phosphorus (BP) as a chemical sensor: CO, CO₂, NH₃, NO, NO₂. In general, black phosphorus exhibits adsorption energies higher than graphene or transition metal dichalcogenides and enables selective responses even at room temperature, which is impossible with other materials like metal oxides. Liquid phase exfoliation is a simple scalable method to produce few-layers phosphorene but the sizes of the flakes are in the order of just few hundreds of nanometers. In order to evaluate the functionalization effect and improve the electrical contacts with the polycrystalline phosphorene for gas sensor applications, we evaluate the effect of nanocomposites by adding carbon nanotubes and mesoporous nickel oxide nanowires. The nanocomposite effect can be explained by the heterojunctions formation and the modifications on the surface potentials. This work opens up opportunities for investigating the performance of BP devices, and shows the prominent advantages of BP as sensing material.

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Preparation and characterisation of graphene-like carbon layer on h-BN nanomesh

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Keywords: surface science, 2D materials, electron spectroscopy, ultra-high vacuum

Using boron nitride in graphene based devices and combination of the properties of the two materials in multilayer structures can enhance the outstanding features of graphene and open new perspectives for example in microelectronics. Graphene (G) and atomic layers of hexagonal boron nitride (h-BN) are complementary two-dimensional materials, structurally very similar but with vastly different electronic properties. Recent studies indicate that h-BN atomic layers would be excellent dielectric layers to complement graphene electronics [1,2]. It is feasible that these can be sequentially grown on metal substrates to create the G/h-BN/metal stacked layers which are certainly useful for applications.

Preparation and investigation of graphene layer on non-metal substrates is one of the exciting areas in surface science nowadays [3]. Moreover, formation of graphene with CVD method on - so called - “white graphene” surface (h-BN) is a great challenge, especially because the substrate boron-nitride layer has “nanomesh” structure [4]. Furthermore, graphene growths on clean Rh(111) resulted also a non-planar 2D carbon layer [5].

In our recent project we investigated the adsorption properties of benzene on the h-BN/Rh(111) surface layer at low and at high temperatures. However, according to the adsorption of benzene on 1000K measurements, we can say that we developed a graphene-like carbon structure on the surface of h-BN/Rh(111) without the removal or destruction of the h-BN film.

Oxidation of the carbon layer resulted CO production in agreement with TPD measurements and the complete recovering of h-BN without defects, analysed by CO titration.

Our results evidenced directly by Auger Electron Spectroscopy (AES) method and indirectly by High Resolution Electron Energy Loss Spectroscopy (HREELS) and Mass Spectrometry (MS)

Acknowledgments

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Synthesis temperature dependence of oxygen reduction activity of Pt/Nitrogen-doped graphene composite

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Keywords: PEMFC, AMFC, ORR, nitrogen-doped graphene, platinum nanoparticle

Excess use of non-renewable energy resources is a serious environmental problem nowadays. Fuel cells can be a promising alternative as they provide rather clean energy and they can be used for various purposes in many sizes. Generally, platinum nanoparticles are used on carbon black support which is an expensive and easily degradable catalyst. Nitrogen-doped graphene support can be an alternative solution with various advantages which improves the ORR efficiency of the dispersed platinum.

Our aim was to optimize the synthesis temperature of a Pt/Nitrogen-doped graphene composite with reduced platinum content and to examine its oxygen reduction activity. A mixture of platinum (II)-acetylacetonate and graphene oxide was thermally treated at three different temperatures between 500 and 700 °C. The resulting material was examined by several characterization techniques: thermogravimetry (TG) was used to determine the platinum content of the samples, transmission electron microscopy (TEM) were applied to examine the graphene sheets and platinum particles, and X-ray photoelectron spectra (XPS) was taken to determine the physical states of graphitic materials and the oxidation state of Pt. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were performed in a three-electrode cell in oxygen saturated 0.1 M HClO₄ and 0.1 M KOH solution by a rotating disk electrode (RDE) at different rotation rates to see the electrochemical behavior of the samples in acidic and alkaline media, compared to a conventional Pt/CB catalyst. Based on the limiting current densities, onset potentials and electron transfer numbers from RDE measurements, the composite annealed at 600 °C and 700 °C exhibited the highest ORR activity in acidic and alkaline medium, respectively.

Acknowledgement

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Interaction of Au, Rh and Au-Rh alloys with the Hexagonal Boron Nitride monolayer studied on Rh(111)

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Keywords: 2D material, hexagonal boron nitride, nanoclusters, nanomesh

Two dimensional monolayers (MLs) of hexagonal boron nitride (h-BN) are promising insulator components for nanoelectronics. The h-BN monolayer has a similar structure and lattice constants as those of graphene. On Rh(111) surface, monolayer h-BN forms a periodically corrugated surface structure, called “nanomesh” [1,2]. This phenomenon allows its application as a nanotemplate [3].

Here we report on the growth of gold and rhodium on the h-BN/Rh(111) surface and on subsequent thermal effects studied by STM, XPS and LEIS. The latter technique reveals the elementary composition of the outermost atomic layer. The h-BN monolayer was formed on Rh(111) by the decomposition of borazine (BAz) at high temperatures (1000 K). Gold forms 1-2 atomic layer thick nearly 2D nanoparticles, when it is evaporated in small amounts (~0,15 ML) on the nanomesh at 300 K. At higher coverages, the growth is strongly 3D. The gold peak was observed at a rather low position (83.7 eV), indicating significant electronic interaction either with h-BN. Indeed, previous density function theory (DFT) calculations indicated an electron transfer from boron nitride to gold [4,5]. The intercalation of gold is the dominant process upon stepwise thermal annealing to 1050 K, but agglomeration and evaporation also occur to a limited extent. Interestingly, though gold and rhodium form a surface alloy after intercalation, the presence of ~ 0.15-0.50 ML of Au below the h-BN layer does not significantly influence the nanomesh structure. At higher gold doses a partial or full flattening of the nanomesh was observed.

We also investigated the growth of h-BN on Au-Rh alloyed surfaces varying the gold content until 4 ML. In these measurements gold was evaporated on Rh(111) at 500 K, followed by annealing at 1000 K for 5 min. Subsequently, the surface was gradually exposed to BAz at 1000 K. The exposure was increased until the whole metal surface was covered by h-BN, as shown by LEIS, but not above 260 L. Decomposition of BAz on the alloyed surface led to the attenuation of both Rh and Au LEIS (normalized) intensities and Au signal slowed down with increasing Au content. It was shown by STM measurements that up to a gold coverage of to 0.5 ML, the nanomesh structure is only slightly disturbed, but larger parts are flattened at higher Au doses.

LEIS studies on the growth of rhodium on h-BN/Rh(111) indicated a predominantly 3D growth, similar to the gold case. When small amounts of rhodium (up to 1 ML) were depos-

ited on h-BN/Rh(111), intercalation was nearly complete upon annealing to ~ 900 K, while dewetting of the h-BN layer set in at ~ 1050 K. At higher rhodium doses, complete intercalation could not be reached at any temperatures.

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Iron-nitride/nitrogen-doped graphene composite: a non-noble metal catalyst for the oxygen reduction reaction

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Keywords: oxygen reduction reaction, electrocatalysis, iron-nitride, nitrogen-doped graphene, fuel cell

Fossil fuels are disadvantageous both economically and environmentally and could be replaced by fuel cells. There are a number of factors limiting the widespread adoption of fuel cells for example the use of platinum as catalyst for the oxygen reduction reaction (ORR) on the cathode side. Platinum is a highly effective catalyst but it is costly and sensitive to the presence of pollutants like methanol. Thus, it is an important task to find a catalyst that is available in larger quantities, cheaper and more durable. Nitrogen-doped graphene proved to be a highly efficient, selective and durable catalyst in the oxygen reduction reaction. Its efficiency can be further increased by mixing it with metals. Transition metal nitrides like iron-nitride are adequate for this purpose as they have their own catalytic activity that can be further improved by mixing them with nitrogen-doped graphene. Our research objective was to produce non-noble metal oxygen reduction catalysts with high catalytic activities. For this purpose, iron-nitride/nitrogen doped graphene composites were synthesized from lyophilized mixture of graphene oxide and iron-acetylacetonate by high-temperature annealing in ammonia. To determine the optimal composition of the catalyst we had produced composites containing different quantities of iron-nitride between 5 wt% to 50 wt%. Composite morphology was examined with transmission electron microscopy, the crystallinity with X-ray diffractometry and the chemical composition with X-ray photoelectron spectroscopy. The electrocatalytic ORR activity was examined in a three-electrode cell, in alkaline media using a rotating electrode. According to the electrochemical investigations, the most promising oxygen reduction catalyst was the one with 20 wt% iron-nitride content. We have also examined the sensitivity of the composite to the presence of methanol with chronoamperometric measurements. Based on our results, our composite, unlike the currently used platinum/carbon black catalysts, is not sensitive to methanol contamination, thus can be used in direct methanol fuel cells.

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T03: Composite materials

Polymer filler material tailored wetting of composite surfaces

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To achieve extreme wetting properties, the adequate surface roughness is a crucial factor. [1,2]. The incorporation of semiconductor photocatalytic particles as polymer filler in an appropriate polymer is expected to create antimicrobial and self-cleaning properties, which would extend its field of application [3]. It is known in the literature that many efforts have been made to develop an artificial superhydrophobic surface by mimicking the lotus leaf structure [4]. The second class of self-cleaning surfaces is photocatalytic coating which can chemically degrade organic materials when exposed to light, a process known as “photocatalysis” [5].

In this work we implemented the synthesis of photoreactive hybrid thin layers with tunable wetting properties. The incorporation of plasmonic Ag-TiO₂ particles into the polymer matrix was ensured the adequate surface roughness of the polymer layer. Beside the structural and wetting characterization of the thin films, the photocatalytic properties of the layers were measured at S/G and S/L interface, as well. At S/L interface the photocatalytic efficiency was dependent on the polarity of the used model pollutants: the superhydrophobic thin film was photodegraded only the organic SUDAN IV dye solution. These dual photocatalytic and adjustable wetting properties of the prepared hybrid layers could be interesting at the area of water treatment, where the polarity of the pollutants varies on a wide scale. Moreover, it was also presented that the surface roughness of a composite thin film can be also induced by external stimuli.

Acknowledgements

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Computational design of new high temperature superconductors at various pressures

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Hydrogen-rich hydrides attract great attention due to recent theoretical [1] and then experimental discovery of record high-temperature superconductivity in H_3S ($T_c = 203$ K at 155 GPa [2]). Here we perform a systematic evolutionary search for new phases in the Fe-H [3], Th-H [4], U-H [5] and other numerous systems under pressure [6] in order to predict new materials which are unique high-temperature superconductors.

We predict new hydride phases at various pressures using the variable-composition search as implemented in evolutionary algorithm USPEX [7-9]. Among the Fe-H system two potentially high- T_c FeH_5 and FeH_6 phases in the pressure range from 150 to 300 GPa were predicted and were found to be superconducting within Bardeen-Cooper-Schrieffer theory, with T_c values of up to 46 K. Several new thorium hydrides were predicted to be stable under pressure, including ThH_3 , Th_3H_{10} , ThH_4 , ThH_6 , ThH_7 and ThH_{10} . $\text{Fm}\bar{3}m$. ThH_{10} was found to be the highest-temperature superconductor with T_c in the range 221-305 K at 100 GPa. Actinide hydrides show, i.e. AcH_{16} was predicted to be stable at 110 GPa with T_c of 241 K.

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Preparation of composite layers to enhance surface roughness durability

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In recent years, superhydrophobic surfaces ($\Theta \geq 150^\circ$) gained much attention from material scientists due to their self-cleaning and corrosion-resistant properties. Superhydrophobic behaviour is mainly associated with the dual-scale (micro and nano) roughness of originally hydrophobic surfaces, which are vulnerable to mechanical and chemical damage due to their fine nature. In order to make an effective, commercially applicable superhydrophobic coating, the provision of durable or renewable surface structures is crucial.

In this work, we introduce a simple preparation method of superhydrophobic PDMS-based oleogel systems with self-healing ability. The three-component PDMS/silicone-oil/dodecyl-trichlorosilane oleogel layers possess moisture-sensitive surface-regeneration capability and microscale roughness. The nanoscale roughness was achieved by the incorporation of 25 wt% visible light-active plasmonic Ag-TiO₂ photocatalyst nanoparticles ($d_{\text{prim.}} = 50$ nm) into the oleogel matrix.

The resulting micro-, and nanostructured superhydrophobic layers were proven to be effective during EtOH (g) degradation tests at the S/G-interface.

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Structural characterization of composite materials by small-angle X-ray scattering and computed tomography

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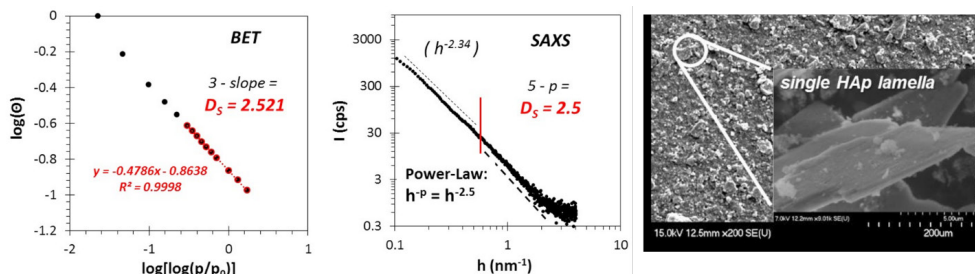
Keywords: computed tomography, CT, SAXS, nanocomposites, photocatalysis

In this study small-angle X-ray scattering (SAXS), N₂ adsorption and computed tomography (CT) techniques are compared as appropriate methods for the characterization of the structure and surface properties of different type nanostructured materials. The surface roughness can be quantitatively characterized by a well-known mathematical concept, namely the non-integer dimensions or fractals.

In this work TiO₂/Hydroxyapatite (HAp) nanocomposites were investigated. Both the TiO₂/ HAp composites and the TiO₂/ polymer hybrid materials are separately well known in the literature, however, here we present that the incorporation of bacterial adhesive HAp lamellae in the TiO₂/ polyacrylate hybrid thin films improve the photocatalytic and antibacterial properties of the composite layers.

SEM, EDX and SAXS measurements proved the homogeneous distribution of TiO₂ particles on the surface of HAp lamellae. This enhanced photoreactive surface and higher TiO₂ accessibility were also proved by the photocatalytic and antibacterial measurements. We show that the catalytic properties of a semiconductor particle may be significantly influenced by the physical (not only the chemical) surface properties, so this study attempts to look for correlation between the surface fractal properties and catalytic activity.

Figures



Double logarithmic plot of the N₂ adsorption isotherm, SAXS curve and SEM image of TiO₂/HAP nanocomposite for the determination of the surface (fractal) properties

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T04: Environmental, health, economic and legislative aspects of nanotechnology

Colloidal stability of silver nanoparticles in biorelevant conditions

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Keywords: aggregation behavior, green synthesis

Silver nanoparticles (AgNPs) are heavily investigated in biomedicine due to their unique cytotoxic and antimicrobial properties. To assess the potential of AgNPs in therapeutic applications, their physiological effects are widely monitored, however their aggregation behavior in biorelevant conditions is rarely examined even though it can have a profound effect on their biological activity.

Therefore in this work, the colloidal stability of two different silver nanoparticle samples with comparable sizes and morphologies were investigated. Chemically reduced particles stabilized by sodium citrate resulted AgNP@C, while a green synthesis using green tea extract produced AgNP@GT. To assess the effect of the most prominent parameters of biological fluids, different pH values, sodium chloride and glutamine concentrations were used as model compounds, furthermore, to simulate more complex systems, Dulbecco's Modified Eagle's Medium and Fetal Bovine Serum were also investigated. Particle size, morphology and crystallinity were characterized using transmission electron microscopy. Aggregation grade measurements were carried out in a time-dependent manner using ultraviolet–visible spectroscopy and dynamic light scattering.

We demonstrated, that the aggregation behavior of AgNPs is mostly affected by pH and electrolyte concentration, while the presence of biomolecules can improve particle stability due to the biomolecular corona effect. Additionally, we showed that AgNP colloidal stability in complex systems can be estimated by simple compounds like sodium chloride and glutamine. Electrostatic stabilization might not be suitable for biomedical AgNP applications, while green synthesis approaches could offer new frontiers to preserve nanoparticle toxicity by enhancing colloidal stability.

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Insight into the impact of graphene-oxide (GO) nanoparticles on aerobic granular sludge (AGS) under shock loading

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Keywords: graphene-oxide, aerobic granular sludge, wastewater treatment, extracellular polymeric substances

Recently, graphene-based nanomaterials have attracted tremendous research interest due to their unique physicochemical properties that hold great promise in electronics, energy, materials and biomedical areas. Graphene oxide nanoparticles (GO NPs) are one of the most extensively studied graphene derivatives, as a result of the increasing development of GO application and production, there arises a growing concern regarding the risks to biological processes and systems. Wastewater treatment plants will be one of the ultimate repositories for these wastes. The aerobic granular sludge (AGS) wastewater treatment is a new technology where bacteria and fungi form aggregates that have many advantages over conventional activated sludge treatment methods. The granules provide protection and more efficient nutrient uptake for the microorganisms. To date, the effect of shock loading of GO on the performance and microbial activities of AGS still remain unknown.

Therefore, the major purpose of the present study is to assess the effect of shock loading of GO NPs on the biological treatment processes in an AGS bioreactor, furthermore microbial activities and EPS production.

During the experiment synthetic wastewater was applied. A chemical oxygen demand (COD) loading of 3.12 Glucose-COD/(m³*day) was applied, the carbon, nitrogen and phosphorus ratio were set to 100:10:1. The COD, ammonia (NH₃), nitrite (NO₂⁻), nitrate (NO₃⁻) and phosphate (PO₄³⁻) concentrations were measured daily. The amount of extracellular polymeric substances (EPS) and mixed liquor suspended solids (MLSS) were measured weekly. Structure and development of granules were investigated via scanning electron microscopy (SEM). After the granulation occurred, GO was added to the system in different concentrations (5, 15, 25, 35, 45, 55, 65, 75, 85 and 95 mg/L).

The formation of the granules caused a fivefold increase in the sedimentation velocity compared to its initial value. Significant inhibition to ammonia oxidizing rate was observed after exposure to 65 mg/L GO. The ammonia concentration increased from 0.2 mg/L to 0.8 mg/L, while the nitrite and nitrate remained stable (0.09 and 0.3 mg/L). At 95 mg/L GO concentration the ammonia concentration was 4.7 mg/L and the sedimentation ability decreased. The content of polysaccharides remained stable (5.2±0.1 mg/g MLSS) at varying levels of GO NP exposure. However, GO NPs stimulated the secretion of proteins (15±5.1 mg/g MLSS) in contrast with the control of 4.1 mg/g MLSS.

Our results suggest that the GO NPs stimulated the secretion of EPS, especially proteins, which played a vital role in protecting AGS from GO inhibition. Moreover, we demonstrated that addition of GO over 55 mg/L concentration has a negative impact in AGS wastewater treatment system.

Preparation of environmentally benign zero valent iron nanoparticles for removing soil contaminants

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Zero-valent iron nanoparticles (nZVI) prepared by using natural product extracts and their volatile chlorinated organics degradation efficiency is tested on groundwater samples obtained from an actual nanoremediation site. In this work we compared nanoparticles obtained by green tea, coffee and Virginia Creeper extracts

The extract was prepared by boiling tea, Virginia Creeper leaves or ground coffee in 100 mL deionized water, thereafter the extracts were vacuum-filtered and stored in fridge for further use. Synthesis methods utilized technical grade ferric chloride, ferrous chloride, ferrous sulfate and NaOH if it was necessary for maintaining basic environment. For laboratory tests and microscopic (TEM) analysis the as-repared nZVI particles were collected by vacuum filtration, than rinsed three times with deionized water and ethanol. The samples were kept in stray ambient light at room temperature without stirring to simulate field conditions. Samples were analyzed by TEM, oxidation/reduction potential measurement and gas chromatography.

We found that the average particle diameter of the particles was between 125-20 nm depending on the synthesis method. The reductive dehalogenation efficiency of nZVI particles were compared in removing volatile chlorinated organic compounds (VOCs) from groundwater samples obtained from a remediation target site.

We are able to use this procedure to synthesize many other metal nanoparticles, for example gold, silver or copper.

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T05: Novel synthesis methods and applications of nanomaterials

Optimalisation and synthesis of macropore silica hollows with amino groups on the surface

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The spherical hollow nanostructures receive high attention today because of their remarkable physical and chemical properties. Among these materials silica is well known because of its high specific surface area and narrow pore size distribution as well as its high thermal and chemical stability and low toxicity. Because of these properties it can be readily applied by diverse research fields including e.g. drug delivery, catalysis, micro reactor, or adsorption¹⁻³.

In our work we synthesized macropore silica hollows using a polystyrene template method^{4,5}. The template is around 500 nm in diameter and the thickness of the walls is around 40 nm. Earlier we managed to add amino groups to the silica⁶, during this research we optimized the synthesis method to achieve a remarkably high surface density of amino groups (4 groups/nm²). In this contribution we discuss these results as well as the modification of an analytical method⁷ that has allowed us to measure the amount of surface amino groups in an indirect way.

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Oxygen-induced structural transformation of pyrochlore $\text{Ce}_2\text{Zr}_2\text{O}_{7+x}$ to the $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase

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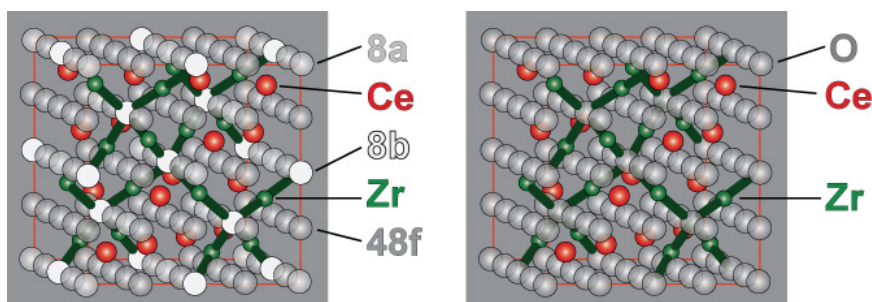
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Keywords: storage capacity, in-situ X-ray diffraction, in situ Raman spectroscopy, Rietveld analysis

The temporary storage of oxygen in a solid catalyst is imperative for many important industrial oxidation reactions in the gas phase, for instance the post-treatment of automotive exhaust gas. A peculiar mixed Ce-Zr (1:1) oxide, the ordered $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase, is a promising catalytic material exhibiting an extraordinarily high oxygen storage capacity (OSC) and high thermal and chemical stability. We elucidated the temperature-dependent transformation between the pyrochlore $\text{pyr-Ce}_2\text{Zr}_2\text{O}_{7.3}$ and $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase upon oxygen uptake by in-situ X-ray diffraction, X-ray absorption and in-situ Raman spectroscopy, providing insights into the electronic and structural changes on the atomic level, which are at the heart of the extraordinarily high OSC. We demonstrate that the Ce^{3+} concentration can be followed during transformation *in-situ* by Raman spectroscopy of the electronic spin flip in the f-shell of Ce^{3+} . The catalytic activity of the $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase has been investigated without an additional active component such as Pt: While the high OSC of the kappa phase is beneficial for the oxidation of CO, the oxidation of HCl turns out to be not affected by the high OSC.



Scheme 1: Structural transformation of $\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$ ($\text{Ce}_{16}\text{Zr}_{16}\text{O}_{56}$, left) to the $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ phase ($\text{Ce}_{16}\text{Zr}_{16}\text{O}_{64}$, right). The O-vacancies in $\text{pyr-Ce}_2\text{Zr}_2\text{O}_7$ are highlighted in white.

Synthesis of Au supported B-doped titanate nanotubes

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Keywords: titanate nanotube, ion-exchange, doping, gold, boron

Titanate nanotubes (TiONT) could be an alternative precursor to prepare doped or metal supported nano-sized titanium-dioxide (TiO₂). TiONT has elongated tubular morphology, layered structure, inner pore channel with 5-6 nm and relatively large specific surface area. TiONT has metastable trititanate (Na₂Ti₃O₇) structure, and its protonated TiONT (H₂Ti₃O₇) easily turns to anatase TiO₂ form by heat treatment around 400 °C, elevated pressure or in acidic media. Generally, TiONT prepared via alkaline hydrothermal method which is a stable and up-scalable synthesis route.

There are several ways in order to prepare doped, impregnated or heterojunction type TiONTs. Both the sodium and protonated form of TiONT has great cation exchange capability. It is easy to donate structure of TiONT with several specimens by ion-exchange. In this case, donor ions have to be positively charged (Bi³⁺, Sb³⁺, Ag⁺, NH₄⁺ ect.). Negatively charged specimens also can doped into TiONT in interstitial position or by oxygen substitution. Elongated titanate nanomaterials (tubes, wires, belts or ribbons). are able to stabilize metal nanoparticles on its surface with good dispersity and relatively homogenous particle size distribution. Metals can be e.g. Pt, Pd, Rh, Cd, and Au, to name a few [1].

TiO₂/Au interfaces is a well-known model system in the field of heterogeneous catalysis. This system is able to water-splitting by light activation and CO₂ hydrogenation by thermic activation, respectively. A considerable study suggest boron addition is affect for the embeddation of Au into B-TiO₂ framework [2]. The as-prepared interfaces increase the water-splitting capability of the catalyst. László et al recently reported about the thermic activated catalytic properties of Au/TiONT in CO₂ + H₂ reaction. They detected only CO as product [3]. Following the above conclusions, a boron doped TiONT framework could promote the embeddation of Au into its structure and improve affect for its CO₂ reduction pathway or efficiency.

In the present study we deal with synthesis and characterization of B-doped Au-decorated titanate nanotubes. We studied the ion-exchanged B³⁺ and Au⁺ specimens by XPS, the optical properties of the B-Au/TiONT by DR-UV-Vis. Structure and morphology were characterized by XRD and TEM.

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Noble metal colloids: development of optical sensors and electrocatalysts

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Gold nanoparticles (Au NPs) and gold nanoclusters (Au NCs) having characteristic plasmonic or highly photoluminescence features have become one of the most important types of nanomaterials that have been extensively investigated in many fields. Due to the size-, shape- and composition-dependent optical properties the Au NPs play an important role in the development of optical biosensors, but the bimetallic nanoparticles are ideal candidates to prepare different catalysts. The sub-nanometer sized Au NCs show unique physical and chemical properties such as well-defined molecular structure, discrete electronic transitions and characteristic size-tuneable photoluminescence which makes them suitable for the development of fluorescent biosensors.

In order to achieve selective detection of metal ions and biomolecules, we produced various noble metal colloidal nanoparticles. In this work we highlighted the fabrications of Au NPs and Au NCs using proteins (bovine serum albumin (BSA); lysozyme (LYZ), gamma-globulin (γ G)), nucleotide (adenosine monophosphate (AMP)) and amino acids (histidine (His); tryptophan (Trp), cysteine (Cys) which result in different nanostructures having tuneable blue, green, yellow and orange emissions. The fluorescent Au NCs were used for selective detection of different transition metal ions (e.g. Fe^{3+}), anions and small drug molecules in aqueous solutions. Moreover, the size-controlled syntheses of various bimetallic NPs are also carried out to fabricate potential electrocatalysts for electrochemical reduction of carbon-dioxide.

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Amperometric determination of hydrogen peroxide by screen printed electrodes modified with nanocomposites of platinum or MnO₂ and multiwalled carbon nanotubes

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Keywords: Pt-MWCNT, MnO₂-MWCNT, screen printed electrodes, amperometry, H₂O₂ and glucose determination

Multiwalled carbon nanotubes (MWCNTs) and nanocomposite made of MWCNTs and Pt or MnO₂ nanoparticles (Pt-MWCNT and MnO₂-MWCNT) were synthesized and characterized by SEM/EDS technique [1]. The prepared nanomaterials were employed as bulk modifiers of screen printed carbon electrodes (SPCE). Cyclic voltammetric and amperometric measurements were performed by the bare SPCE and the modified ones, MWCNT-SPCE, Pt-MWCNT-SPCE and MnO₂-MWCNT-SPCE, to investigate their applicability for the determination of H₂O₂ in slightly alkaline media as supporting electrolyte (phosphate buffer 0.1 M; pH 7.50). The nanocomposite based electrodes showed enhanced analytical performance with significant decrease in overpotential for H₂O₂ responses compared to SPCE and MWCNT-SPCE. Both electrodes, Pt- and MnO₂-MWCNT-SPCE, are suitable for the H₂O₂ determination in sub-millimolar concentration ranges. Moreover, Pt-MWCNT-SPCE and MnO₂-MWCNT-SPCE served to design simple first generation glucose biosensors made from glucose oxidase and Nafion[®].

Acknowledgments

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Wetting and evaporation in the case of Gas Diffusion Layers

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Keywords: fuel cell, gas diffusion layer, carbon materials, wetting, evaporation

Nowadays, the non-renewable energy resources of the world are exhausted. We need to replace some alternative sources. There are many possibilities but our aspiration to develop the fuel cells, through to learn the wetting properties of Gas Diffusion Layers (GDL). The GDL is a part of the fuel cell, which is generally a porous carbon material. It is located on both side of the membrane which separates the anode and cathode side. The main function of this layer is to help the flowing of reactant gases, water or other used solvents. Besides that it possesses hydrophobic properties to avoid of “flooding” because it would be permeable to the gases. Furthermore, it needs to have a good electric-and heat conductivity [1].

During our research, we would like to compare the wetting properties of some various GDLs. The differences between them are thickness, Teflon® content and some of these have or don't have microporous layer. The morphology of GDLs is observed by X-Ray Micro Tomography and the varying surfaces of these were investigated by a Scanning Electron Microscope. Now, the wetting and evaporation processes are presented through the carbon-cloth type GDL.

During the evaporation of the solvent the electrical resistance are changing, the DGL represents a characteristic sign which is the so called evaporation profile (EP) [2]. The EPs are compared to in shapes and sizes which are related to the GDL's and solvents properties. Furthermore the part of the evaporation was examined by infrared (IR) camera and the weight loss was observed by an analytical balance. We could get some information about the wetted area on the GDL and the size of the drop by the IR camera. If we apply these three technics in the same time this could allow learning the behaviour of the GDLs during the wetting. Moreover we get some other information about GDLs by initial and time-varying contact angle measurements. Indirectly, these results could contribute to improve the performance of the fuel cells.

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Influence of an interlayer cation exchange in birnessite and electrochemical activity for oxygen reduction reaction (ORR)

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Keywords: Birnessite, Interlayer cation exchange, electrochemistry, catalyst, ORR

Manganese is one of the most abundant metals and manganese oxide minerals are ubiquitous in natural environments [1]. Manganese oxides, including MnO, MnO₂, and Mn₃O₄, are intriguing materials and have been used in wastewater treatment, heavy metal remediation, photocatalysis, organic dye removal, sensors [2], supercapacitors [3], alkaline and rechargeable batteries [4][5]. Particularly, birnessite-type MnO₂ materials have attracted great interest as supercapacitor in batteries [6] [7] for their high theoretical capacity, environmental benignity, and other special properties. Low cost and high activity electrocatalysts for oxygen reduction reaction (ORR) are necessary for the development of fuel cells and metal-air batteries.

Here we report a development of the simple and cost-effective method to synthesize Fe and Cu intercalated potassium birnessite with a high specific surface area and tested catalytic activity for oxygen reduction reaction (ORR). The intercalation of the cations (K⁺, Fe²⁺, Cu²⁺) was verified by XRD and Raman spectroscopy, the morphology was studied by scanning electron microscopy, the chemical composition was measured by energy dispersive X-ray spectroscopy (EDX), the crystal structure was determined by transmission electron microscopy (TEM), the specific surface area and pore diameter was measured by nitrogen adsorption, the thermal properties were investigated using thermogravimetry, the pH-dependent surface charge and aggregation state were studied by zeta potential measurement and dynamic light scattering (DLS) and electrochemical measurements were performed in a three-electrode cell system. Our study demonstrates a successful intercalation process to produce mixed interlayer cation-birnessite with the increased specific surface area and improved electrocatalytic activity for oxygen reduction reaction.

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Study of oxide bands in p-type nanostructured silicon layers

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Keywords: Porous Silicon, Nanostructures, Impedance Spectroscopy, Oxide

The interest in developing fast and reliable chemical and biochemical sensors in an inexpensive way is something that has attracted a lot of efforts in the last decades [1]. One of the potential material candidates is electrochemically treated silicon to form porous silicon (PSi). This treatment generates silicon nanostructures within the porous matrix [2]. The large area to volume ratio is especially interesting for sensing applications. The main drawback of this material is the fast oxidation that impedes the correct device detecting capability.

This work is devoted to the study of the oxidation dynamics in PSi. Impedance Spectroscopy (IS) technique was applied on nanocrystalline silicon (NCSi) samples after submitting those surfaces to distinct phases of oxidation. Oxide phases were analyzed by Attenuated Total Reflectance in Fourier Transformed Infrared Spectroscopy (ATR-FTIR) and sessile drop Contact Angle (CA) technique. Nyquist plots were produced and studied by fitting the curves to a model containing a network of passive circuit elements. Results indicate a correlation between oxidation evolution (obtained from ATR and CA data) and the equivalent elements extracted from the impedance model, indicating a change in the surface chemistry of the semiconductor surface. This change is attributed to the presence of Si-O bonds that replace the Si-H bonds in the original surface state.

Figures

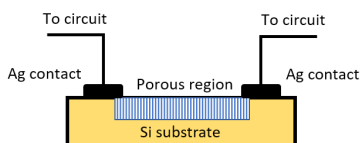


Fig. 1: Schematic cross section of samples prepared for IS measurements.

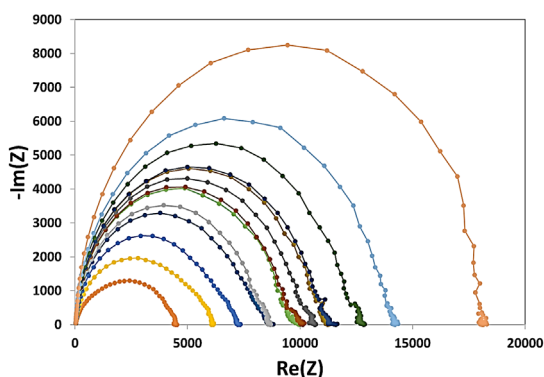


Fig. 2: Typical IS spectrograms showing an evolution in the dynamics of the system, from lower oxidation (smaller curves), to higher oxidation (larger curves).

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Bimetallic Ag-Pd nanoparticles: effect of silver on catalytic activity of palladium

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Keywords: bimetallic nanoparticles, palladium, silver, methylviologen, reduction, hydrogen, catalysis

Studying the properties of bimetallic nanoparticles, which contain the noble metals causes a great interest. This applies in particular to Pt and Pd, due to their exhibited high catalytic activity. However, the high cost of these metals makes researchers look for ways to reduce their content in the catalyst without loss of catalytic activity.

In this work bimetallic nanoparticles were obtained by reduction of Ag⁺ ions on surface of palladium seed. Palladium nanoparticles were obtained by a photochemical method. This method consists in irradiation of the solution of palladium salt and sodium polyacrylate by ultraviolet light. This gives rise to the formation of ultrafine particles with the following characteristics reproducible in repeated experiments: size $d_{\text{TEM}} = 2.5 \pm 0.6$ nm (transmission electron microscopy), hydrodynamic diameter $d_{\text{DLS}} = 12.4 \pm 6.0$ nm (dynamic light scattering), and zeta-potential $\zeta = -52.0$ mV. Under our experimental conditions, sodium polyacrylate serves as not only a stabilizer of nanoparticles, but also it is a «supplier» of organic radicals, which are forming in photolysis and exhibit reducing properties.

Ag-Pd nanoparticles were prepared by saturating a preliminarily deaerated solution, which contained palladium particles, stabilizer (sodium polyacrylate) and a necessary amount of silver salt, by hydrogen. The reduction of silver ions was carried out enough slowly and kinetics of this process was studied by optical method. It has been found that kinetic curves of silver ions reduction are described by the equation of first order reaction.

The reaction of one-electron reduction of methylviologen ions (MV²⁺) with hydrogen in an alkaline medium was carried out to study the catalytic activity of palladium nanoparticles and bimetallic Ag-Pd nanoparticles with different content silver. It is known that this reaction is catalyzed by palladium and yields methylviologen radical cations (MV^{•+}). It has been found that bimetallic Ag-Pd nanoparticles catalyzed the reduction of methylviologen-ions by hydrogen also. However, as silver content in the nanoparticles increases, catalytic activity decreases compared with the catalytic activity of monometallic palladium nanoparticles. Furthermore, appearance of induction period was observed for catalysis bimetallic nanoparticles Ag-Pd. The induction period grows linearly with increasing silver content in mixed nanoparticles.

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One-pot strategy for magnetically modified graphene oxide nanosheets synthesized under mild conditions

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Keywords: graphite oxide, exfoliation, heteroaggregation, iron oxide nanoparticles, magnetic hyperthermia

Composite dispersions of nanostructured materials containing magnetite (Fe_3O_4) nanoparticles (MNPs) and graphene oxide (GO) lamellae have been prepared by a mild and easily upscalable procedure. The charge regulated adhesion of bare MNPs to GO results in the formation of stable and uniform nanocomposite materials in a wide composition range without any preliminary functionalization steps or harsh conditions that may lead to chemical degradation of the graphene-based nanosheets [1]. Owing to the enormous surface area and negative surface charge developed in aqueous suspensions GO particles were able to accommodate MNPs that represent masses up to 50 times larger than the lamellar carbonaceous host. The macroscopic-scale observations and electron microscopy studies suggest that there is a strong interaction between the Fe_3O_4 and the GO surfaces. The oppositely charged GO and magnetite nanoparticles form huge secondary particles in the lower MNP/GO mass ratio region probably due to the bridging of GO lamellae via MNPs. Large variation in the compositions affords highly different nanostructures ranging from “house of cards” arrangement of MNP decorated exfoliated graphite oxide particles at 2/1 and 1/1 GO/MNP ratios to GO nanosheets matrixed into bulk amounts of magnetite at higher loadings. However, as the MNP/GO mass ratio further increases, the average hydrodynamic diameters of dispersed particles successively decrease reaching the submicron scale (from 2700 down to 400 nm), while the zeta potential was -30 mV for pristine GO sheets and it rose above +35 mV with increasing the MNP loading in the pH range of 4.5-6. The potential use of the magnetic nanocomposites was demonstrated by their heating efficiency for a potential future use in hyperthermic cancer therapy [2]. We have found that nanocomposites generated larger heat effects than the suspension containing only MNPs as it was measured 6.8°C and 7.3°C temperature increase for 1/5 and 1/50 GO/MNP, respectively, after 5 minutes of AC magnetic field exposure (109.4 kHz, 24.7 mT).

Acknowledgments

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Synthesis and characterisation of monodisperse platinum nanoparticles with various approaches

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Keywords: nanoparticle, synthesis, synthesis method, platinum

Discovering new alternative catalysts for organic reactions is an important and challenging task. The use of transition metals in these kind of reactions has had success since the beginning of the 19th century, and rapidly gained relevance in the industry. Development of nanostructure related methods can help us to enhance these reactions by reducing the generation of by-products and waste material.

This study showcases various approaches that were developed for the synthesis of nanostructured platinum crystals in a wide range of size (1-100nm). Smaller nanoparticle (1–10nm) synthesis was achieved by the so called polyol synthesis method and was adjusted after the preliminary synthesis results to ensure the product is monodisperse; we used different precursor compounds, and reaction time or temperature schedules. These reactions were carried out under argon atmosphere in ethylene-glycol medium. For particles bigger than 10nm we did reactions that consist of two or three steps, the first step being the synthesis of 5nm “seed” particles. These particles served as the nucleation sites for the large particles (20–50nm). Repeating the process of the second step, using the product of earlier reactions as the nucleation site, we managed to create particles with 80nm average diameter. These reactions require milder reaction conditions compared to polyol reaction, and water is applicable as a medium and solvent.

Characterisation of the nanoparticles involved transmission electron microscopy and dynamic light scattering measurements, these methods have shown the monodisperse size distribution and spherical geometry of the nanocrystals. Our main goal in the future is to make measurements regarding the catalytic activities of the nanoparticles produced by the methods described above.

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Controlled sized platinum nanoparticles supported on H-ZSM-5 catalyst for efficient CO₂ hydrogenation: Role of interfacial sites in high activity

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Keywords: Carbon dioxide, Hydrogenation, Platinum nanoparticles, ZSM-5

In the recent decades, drastic changes in the industrialization and fast development of metropolises have resulted in boosting the level of greenhouse gases in the Earth's atmosphere. This unbalanced carbon problem is threatening the sustainable development of our economy and society¹. At the same time, the ambiguity between the increasing energy requirement and declining non-renewable fossil fuel resources could cause a foreseeable crisis to mankind. Carbon dioxide (CO₂) is the second most effective greenhouse gas. The utilization of CO₂ as a C1 building block is an outstanding approach towards decreasing the global CO₂ emissions and additionally initiates a new sustainable direction for producing beneficial feedstock chemicals and fuels^{2,3}.

Catalytic systems prepared by controlled processes play important role in the utilization of CO₂ via catalytic hydrogenation to produce useful C1 chemicals (such as CO, CH₄ and CH₃OH). Size controlled Pt nanoparticles were prepared by a polyol method and deposited on H-ZSM-5 (SiO₂/Al₂O₃ = 30, 80 and 280) zeolite supports. The prepared catalysts were tested for the CO₂ hydrogenation at T = 473–873 K and ambient pressure, with CO₂/H₂ = 1:4. Controlled sized Pt nanoparticles boosted the catalytic activity of the pure H-ZSM-5 zeolites resulted in ~16 times higher CO₂ consumption rate. The activity were ~4 times higher and CH₄ selectivity at 873 K was ~12 times higher over 0.5 % Pt/ H-ZSM-5 (SiO₂/Al₂O₃ = 30) compared to 0.5 % Pt/H-ZSM-5 (SiO₂/Al₂O₃ = 280). In situ DRIFTS and NH₃-TPD revealed that the acid centums (Lewis and Brønsted) of zeolits played a key role in the CO₂ hydrogenation.

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Preparation and characterization of PLGA nanoparticles for drug delivery

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Keywords: PLGA, drug delivery, ketoprofen

Our aim was to prepare nanoparticles (NPs) from PLGA - Poly(lactide-*co*-glycolide) copolymer as potential drug carriers for neurodegenerative diseases. The polymers were prepared from lactide and glycolide dimers at different initial ratio by ring-opening polymerization (ROP) [1]. By varying the polymer composition, the hydrophobic character can be tuned, thus encapsulation efficiency and drug release can be optimized. Prior to encapsulation the properties of the synthesized polymers and the potential pharmaceutical carriers were discussed in great detail.

The change in hydrophobicity was detected by contact angle measurements on glass surface and successfully decreased from 74.6° for the pure PLA (polylactide) to 68.5° for the PLGA65 (lactide:glycolide = 65:35) sample. The molar mass of prepared PLGA polymers is rarely discussed in publication, 93 kDa value was obtained for PLGA65 and 70 kDa for PLGA75, respectively. Nanoparticles were prepared from the polymers by three different methods, nanoprecipitation [2], emulsion and by the w/o/w double emulsion method [3]. During stabilization, various stabilizing agents like ionic and non-ionic surfactants and macromolecules were applied. The average particle size and size distribution was determined through both electron microscopy (TEM, SEM) and dynamic light scattering (DLS) measurements. The slightly higher NP size in case of PLGA75 relative to PLGA65 also suggests increased hydrophobicity independent of the stabilizing agent. The smallest NPs with most monodisperse size distribution was obtained for the Pluronic stabilized NPs ($d_{AV} \approx 180$ nm) prepared by nanoprecipitation method.

A model non-steroidal anti-inflammatory drug (NSAID), ketoprofen (KP) were applied to test the PLGA75 and PLGA65 nanoparticles as potential drug nanocarrier. The drug release from the NPs was followed by detection of the change in KP spectra by UV-Vis spectrophotometry. The obtained profiles were evaluated by different kinetic models, and the kinetic parameters were calculated.

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Ketoprofen drug encapsulation in hyaluronic-acid and chitosan-based nanoparticles

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Different types of hyaluronic acid (HA) and chitosan-based colloidal drug delivery systems were prepared for the encapsulation of ketoprofen (KP), a non-steroidal anti-inflammatory drug (NSAID), as the model drug molecule. Cross-linked derivatives of HA were synthesized at cross-linking ratio of 50, 75 and 100 % to decrease the extremely hydrophobic nature of HA to encapsulate a hydrophobic drug. In addition, to achieve the above mentioned goal, the hydrophobized variants of HA have also been produced by modification with positively charged cetyltrimethylammonium bromide (CTAB) surfactant at different HA monomer/CTAB mass ratios. Rheological investigations were performed to characterize the change in HA structure due to the cross-linking or surface modification. The original coherent gel-like structure of the HA changes into an incoherent colloidal system after modification. The increase in cross-linking ratio resulted in the formation of nanoparticles (NPs) in the range of ca. 40-110 nm, while with an average diameter of ~ 100-120 nm was obtained for HA/CTAB particles. Chitosan-based, HA-covered NPs were also synthesized at different composition to combine their favorable properties as potential pharmaceutical carriers. The detailed characterization of the thus prepared composites were carried out.

Depending on their chemical structure the KP molecule bound to these modified HA-based carriers at different degrees. Based on the release profiles of the different systems it can be concluded that nearly 70 % of the encapsulated KP molecules dissolve from the totally cross-linked HA systems but the release rate of KP is about 20 % (after 8h) from the CTAB-modified colloidal system at HA monomer/CTAB 1:0.8 mass ratio. The increase in the amount of CTAB turned the release of KP to diffusion and erosion controlled way.

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