

49th Heyrovský Discussion

Electrochemical Interfaces at the Nanoscale

Book of Abstracts



May 29th – June 2nd, 2016

The 49th Heyrovský Discussion 2016 was held at the Conference centre in chateau Třešť in town Třešť in the Czech Republic, from May 29th to June 2nd, 2016.

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49th Heyrovský Discussion

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Organizers

Ladislav Kavan and Pavel Janda

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PROGRAMME

Sunday, May 29th			
14:00	Registration in the entrance hall of the J. Heyrovský Institute		
15:00	Departure of a special bus from the J. Heyrovský Institute (Dolejškova 3, Prague 8 – Kobylisy)		
17:00	Arrival at the Castle Třešť, Registration		
18:30	Welcome drink		
19:00	Dinner		
Monday, May 30th			
7:00-9:00	Breakfast		
9:00	Morning session:		
	Opening of the Discussion L. Kavan		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:05-10:05	P. Schmuki	U. Diebold	Water on Single-Crystal Metal Oxide Surfaces, Studied at the Atomic Scale.
10:05-10:35		<u>T. Berger</u>	Electron Traps at the Semiconductor Oxide/Electrolyte Interface.
10:35	Coffee break		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
11:05-11:25	T. Berger	K. Minhová Macounová (P.Krtil)	Hypochlorite Oxidation on Nanocrystalline RuO ₂ - Unwanted Parasite or Solution for the Planet?
11:25-11:45		P.Dytrych	Shape Selective Photoinduced Electrochemical Behaviour of Thin ZnO Layers Prepared by Surfatron.
11:45-12:15		<u>M. Kalbáč</u>	Spectroscopy, Chemistry and Spectroelectrochemistry on Graphene.
12:15-12:35		V.Valeš	Functionalized Graphene-Enhanced Raman Scattering
12:45	Lunch		
14:30	Afternoon session:		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
14:30-15:30	P. Kluson	E. Frackowiak	Mysterious Carbon/Electrolyte Interface at the Nanoscale.
15:30-16:00		<u>O. Frank</u>	Charge and Stress Transfer in Deformed 2D Materials.
16:00	Coffee break		

Monday, May 30th			
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
16:30-17:00	E. Frackowiak	<u>P.Janda</u>	Should Electrochemists Be Aware of Surface Gaseous Nanobubbles?
17:00-17:20		J.Klíma	Do Nanobubbles Exist in Bulk Liquids? Can We Prepare Them on Demand?
17:20-17:40		S. Hasoň	How Carbon Nanostructures Based on Graphene and its Oxides Influenced the Electrochemical Detection of Purine Metabolites and Amino Acid Tryptophan in Clinical Body Fluid Samples.
18:00	Concert of Chamber music		
19:00	Dinner		

Tuesday, May 31st			
7:00-9:00	Breakfast		
9:00	Morning session:		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:00-10:00	V. Mortet	Ch. Nebel	Diamond for Bio- and Electrochemical Applications.
10:00-10:20		H.Krýsová	Diamond Photocathodes for Dye-Sensitized Solar Cells.
10:20	Coffee break		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
10:50-11:20	Ch. Nebel	<u>V. Mortet</u>	Structural and Electrochemical Characterisation of Thick Porous Boron Doped Nano-crystalline Diamond/SiO ₂ Nanofiber Composite Fabricated by Plasma Enhanced Chemical Vapour Deposition.
11:20-11:40		Z. Vlčková Živcová	Electrochemical Characterization of <i>p</i> - and <i>n</i> -type Doped Diamond Electrodes.
12:00	Lunch		
14:00	Walking (optional biking) trip Třešť to castle Roštejn and back (16 km)		
19:00	Garden Barbecue Party		

Wednesday, June 1st			
7:00-9:00	Breakfast		
9:00	Morning session:		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:00-10:00	J. Krýsa	P. Schmuki	TiO₂ Nanotube Arrays: Latest Features and Applications
10:00-10:30		<u>J. Macák</u>	Towards Functionalization of TiO ₂ Nanotubular Layers by Secondary Materials.
10:30	Coffee break		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
11:00-11:30	U. Diebold	<u>J. Krýsa</u>	Titania and Hematite Photoanodes for Photoelectrochemical Hydrogen Production.
11:30-12:00		<u>P. Krtil</u>	Water Splitting on Illuminated Semiconductors – Surface Sensitivity of the Hydrogen and Oxygen Evolution on Titanium Dioxide Polymorphs.
12:00-12:20		Š. Kment	Enhanced PEC Water Splitting Efficiency of Highly Textured Hematite Photoanodes.
12:30	Lunch		
14:30	Afternoon session:		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
14:30-15:30	M. Nesládek	J. Janata	Atomic Metals
15:30-15:50		Š. Lachmanová	Expanded Branched Pyridinium Derivatives: Structure – Single Molecule Conductance Relationship.
15:50-16:10		V. Kolivoška	Investigation of Electron Transport through Tower-Shaped Molecular Conductors Based on the Tetraphenylmethane Tripod Stand.
16:10	Coffee break		
16:40-17:10	J. Janata	<u>M. Nesládek</u>	Beyond Optical Detection of Spins in Diamond and Application to Sensors
17:10-17:40		<u>F. Calle Vallejo</u>	Do Defects Increase or Decrease the Oxygen Reduction activity of Platinum?
17:40-18:00		M. Prokop	Oxygen Reduction on Pt Catalysts in H ₃ PO ₄ Electrolyte at Elevated Temperature.
18:00-18:20		M. Pižl	A Quantum Chemical Study of the Ethylene Oxidation at Nanostructured Gold and Platinum Electrodes.
18:20	Closing Remarks		
19:00	Banquet		

Thursday, June 2nd

from

7:00 Breakfast

9:30 Departure of charter bus to Prague

12:00 Expected arrival to the J. Heyrovský Institute

Keynote

Invited

KEYNOTE LECTURES

WATER ON SINGLE-CRYSTAL METAL OXIDE SURFACES, STUDIED AT THE ATOMIC SCALE

ULRIKE DIEBOLD

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Water on oxides is obviously a relevant system to study: under ambient conditions, virtually every surface is oxidized and covered with a film of water. From both fundamental and applied point of view it is interesting to understand the behavior of the first layer of water in contact with such surfaces at the molecular scale.

In the talk I will discuss well-characterized, single-crystalline oxide surfaces (e.g., TiO₂, ZnO, Fe₃O₄, and SrO- and CaO terminated ruthenates) covered with fractional monolayer coverages from the gas phase. With Scanning Tunneling Microscopy (STM) experiments under ultrahigh vacuum (UHV) conditions with area-averaging spectroscopies to observe intricate structures of water layers, and the dynamic behavior of single molecules, and we resort to collaborative DFT calculations to explain our experimental results. Defects are often reactive centers, and O vacancies invariably lead to water dissociation. The delicate balance of H-bonding between surface O and the O atom in the neighboring water molecule determines the rich structural varieties that evolve in the first monolayer.

I will also discuss the challenges (and first glimpses of success) of trying to find out how these surfaces change when immersed in liquid water, and of performing atomically-resolved STM studies under such conditions.

MYSTERIOUS CARBON/ELECTROLYTE INTERFACE AT THE NANOSCALE

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Electrochemical capacitors as attractive power sources occupy a significant area for hybrid vehicles, storage of renewable energy, back-up memory systems... Most of them are based on organic electrolytic medium, however, interest for aqueous electrolyte is growing considerably because of its low cost, easier assembly process, better conductivity than organic solutions, safety and environmental issues. The major disadvantage of capacitors working in aqueous electrolytes is their low maximum operating voltage (~1 V) which directly limits their energy output. Recently, a maximum capacitor voltage in neutral electrolyte (mainly Li₂SO₄-based) within 1.5 to 2.2 V is reported being strongly affected by current collector, electrode material but also investigated method [1-7]. In this work we are focused on exploring two pseudocapacitive effects to reach high voltage capacitor.

Activated carbon with developed surface area Kuraray YP-80 (2429 m²/g) was used for preparing electrodes. Both electrodes were soaked in different electrolytes, i.e. 1M Mg(NO₃)₂ for negative electrode and 1M KI for positive one. 1M KNO₃ served as an electrolyte for the separator wetting. The novelty of our present system is an additional pH change of electrolyte solution to acidic one (pH=2) for positive electrode and to alkaline pH equal to 10 for negative side. In such a hybrid configuration, two different charge storage phenomena are combined: an electrostatic on negative electrode with significant potential change during charging/discharging and redox reaction on positive electrode with slight potential dependence. Electrochemical hydrogen storage has to be considered as a source of capacitance on negative electrode. An advantage of this phenomenon is the shift of the hydrogen evolution potential; it can be exploited to increase the maximum electrochemical window of aqueous-based supercapacitors. Pseudocapacitive effects of I⁻/I₂ redox couple in such hybrid configuration play a crucial role.

Galvanostatic charging/discharging and floating tests at 1.8 V were realized and good cycling performance was proved (over 20 000 cycles with 97% capacitance retention). Separation of two electrolytes plays a crucial role in capacitance retention and enhancement energy/power performance. Some attention was also devoted to estimate the harmful role of investigation method on cell pressure, volatile products, carbon corrosion etc. It seems that galvanostatic cycling is more aggressive method for the electrode integrity than floating and such conclusions were drawn from different charging/discharging tests with *in situ* mass spectrometry coupled [7].

Novel concept of electrochemical capacitor operating in different separated electrolytes has been proved. Two pseudocapacitive phenomena, i.e. hydrogen storage on the negative electrode and efficient iodine/iodide activity on the positive electrode were beneficial for high voltage capacitor operation. Proposed concept allows a capacitor voltage of 1.8 V to be reached. Hence, high power and energy performance (~ 20 Wh/kg at 1 kW/kg) was obtained. Long-term stability of capacitors has been confirmed by floating and galvanostatic tests.

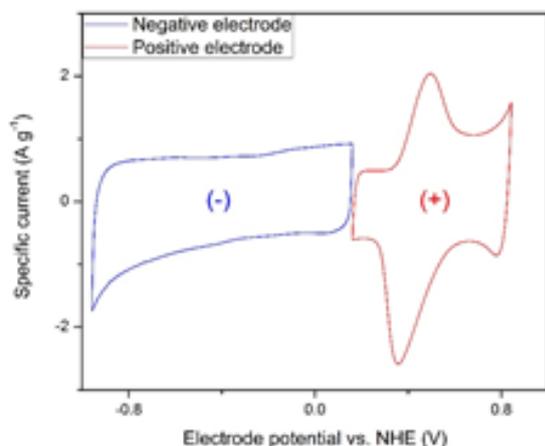


Fig. 1 Voltammograms of capacitor electrodes operating in various separated electrolytes:

(-) 1M $\text{Mg}(\text{NO}_3)_2$ pH=10 // 1M KI pH=2 (+)

Scan rate: 1mV/s

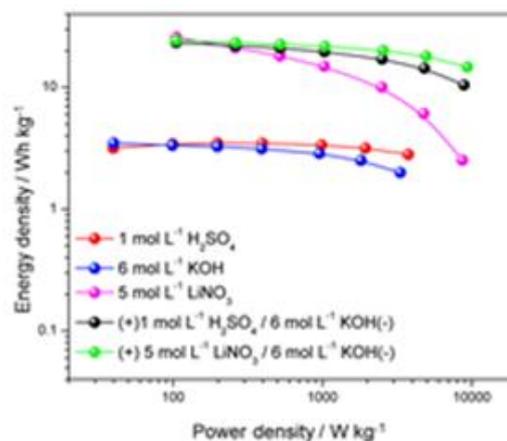


Fig. 2 Ragone plot for the various hybrid capacitor systems

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- [7] M. He, K. Fic, E. Frackowiak, P. Novak, E. J. Berg "Ageing phenomena in high-voltage aqueous supercapacitors investigated by in situ gas analysis" *Energy Environ. Science* 9 (2016) 623-633

ATOMIC METALS

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Reactivity of metals is governed not only by their nature, but also by their size. Electrochemical method of preparation of metals in atomic form, using polyaniline as the isolation matrix has been developed. By this method un-capped clusters of pure metals Au_N , Pd_M and of metal alloys Au_NPd_M consisting of up to 7 atoms have been prepared. The ionization energy of such atomic size clusters exhibits a characteristic “odd-even” pattern in excess of 2eV for atomic Au_N . It is governed by the quantum mechanical pairing of free electrons in Au. Likewise, the HOMO-LUMO gap energy of Pd_2 exhibits theoretically predicted peak value. It has been found that order in which the atomic heteroatoms are deposited affects their catalytic activity. Electrooxidation of lower aliphatic alcohols in strongly alkaline medium, as well as infrared spectra of the composites follow the theoretically predicted patterns and confirm the existence of atomic metal moieties in the matrix.

DIAMOND FOR BIO- AND ELECTROCHEMICAL APPLICATIONS

C.E. NEBEL, FANG GAO, G. LEWES-MALANDRAKIS, W. MÜLLER-SEBERT

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Electrochemical applications of materials are challenging as these devices need to work in aggressive media ranging from acids to ionic liquids to physiologic buffer solutions. Most of established substrates do not possess long term chemical stability, giving rise to decomposition, poisoning and surface fouling.

In addition, future technologies will require integration into electrochemical platforms like super-caps, bio-sensors, fuel cells and water-splitting devices for energy storage and conversion, for sensing and for catalytical material processing.

In this presentation we will introduce diamond which can become a promising candidate for a variety of electrochemical application [1-3]. Diamond shows superior properties for use in applications as indicated above. Diamond can be grown on large area in poly- or nano-crystalline form, either insulating (transparent) or metallically conductive using boron as p-type dopant. Diamond electrochemical surfaces can be flat and smooth; however, by top down etching or bottom up growth, we have introduced diamond wires and foam for surface enlargements in super-caps or membranes in bio-fuel cells. The surface of diamond can be terminated with a variety of atoms or molecules to control the wetting properties (hydrophobic, hydrophilic) and to tune the electron affinity with respect to electrochemical potentials. In addition, hydrogen has been shown to terminate the surface carbon bonds close to perfect which results in an unpinned surface Fermi level which can align with the chemical potential of buffer solutions. The electrochemical potential-window of diamond is significantly larger and the background current within this regime considerably lower than conventional materials. Diamond is known to be biocompatible and has therefore a potential for “in-vitro and in-vivo” electronic applications. During recent years a variety of surface modifications have been introduced and surfaces have been functionalized with DNA, enzymes and proteins. It has been demonstrated that the bonding of bio-molecules to diamond is chemically more stable than to other substrates.

In this presentation we will introduce and discuss these properties, the realization of nano-textures, nano-wires and foam using self-organized particle-formation as templates for etching or overgrowth. We will show applications of diamond in ultra-micro- and nano-electrode arrays, in scanning electrochemical microscopy tips (SECM) and in super-caps as surface enlarged electrode. We will show that diamond surfaces can be hydrogen terminated to realize fast electron exchange rates using an electrochemical schema.

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TiO₂ NANOTUBE ARRAYS: LATEST FEATURES AND APPLICATIONS

PATRIK SCHMUKI

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TiO₂ nanomaterials have over the last 30 years attracted tremendous scientific and technological interest. Main research direction using TiO₂ in functional applications are still the use in photocatalysis e.g. for the direct splitting of water into H₂ and O₂ to generate the potential fuel of the future, hydrogen, or the use in Grätzel type solar cells. In order to achieve a maximum turn-over rate (by creating a high surface area), usually nanoparticles are used either suspended or compacted to a photoelectrode. Over the past decades various 1D and highly defined TiO₂ morphologies were explored for the replacement of nanoparticle networks and were found in many cases superior to nanoparticles. Nanotubes or wires can be grown by hydrothermal or template methods, or even more elegantly, by self-organizing anodic oxidation. The latter is not limited to TiO₂ but to a full range of other functional oxide structures on various metals and alloys can be formed. These advanced and doped morphologies can be grown on conductive substrates as ordered layers and therefore can be directly used as functional electrodes (e.g. photo-anodes). The presentation will focus on these highly ordered nanotube arrays of TiO₂ and discuss most recent progress in synthesis, modification and applications.

References (reviews):

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INVITED LECTURES

ELECTRON TRAPS AT THE SEMICONDUCTOR OXIDE/ ELECTROLYTE INTERFACE

THOMAS BERGER, AUGUSTO MÁRQUEZ, GILLES R. BOURRET, OLIVER DIWALD

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The macroscopic properties of semiconductor oxide films depend in a complex way on the bulk and surface properties of the primary building blocks and on the way these crystallites are merged to form the porous network. The complexity of these high surface area materials increases further under application-relevant conditions in the presence of a surrounding electrolyte.

Solid/solid interfaces between semiconductor oxide particles (TiO_2 , WO_3) constitute bottlenecks for charge transport and/or charge separation. In WO_3 nanoparticle films, for instance, the detrimental effect of these bottlenecks can be mitigated by the photoinduced or electrochemical in situ generation of $(e^-)(H^+)$ centers, which diminishes inter-grain resistance for the majority carrier transport and leads possibly to the deactivation of recombination centers. Double injection of electrons and protons into the oxide structure at potentials $E_{\text{Ag}/\text{AgCl}} > -0.05$ V gives rise to an almost 3-fold, transient increase of the photocurrent. Strong electrochemical doping at $E_{\text{Ag}/\text{AgCl}} < -0.05$ V, on the other hand, is associated with a major structural modification of the oxide at the solid/electrolyte interface and leads to tungsten bronze formation. Although charge accumulation shows complete reversibility with respect to anodic polarization, electrodes suffer a significant decrease in photoelectrocatalytic activity. Obviously, charge accumulation/extraction cycles lead to the irreversible formation of defects in the thin film, which may act as recombination centers. The dynamic change of thin film properties associated with the doping process is tracked by a combined ATR-IR- and DR-UV/Vis-spectroscopic and electrochemical approach, which allows resolving on the electrochemical potential scale the beneficial and detrimental effects of defects in semiconductor oxide thin films.

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- [2] T. Berger, O. Diwald *Springer Series in Surface Sciences* 58 (2015) 273.

DO DEFECTS INCREASE OR DECREASE THE OXYGEN REDUCTION ACTIVITY OF PLATINUM?

FEDERICO CALLE-VALLEJO^a, MARCUS POHL^b, DAVID REINISCH^b, DAVID LOFFREDA^c,
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The role of defects on the oxygen reduction reaction (ORR) catalyzed by platinum is still a matter of debate, as contradictory but reproducible observations are available in the literature. On the one hand, it is well known that stepped Pt(111) electrodes are more active than the pristine ones and the maximum enhancement is found at short terrace lengths with 3-4 Pt atoms [1-3]. On the other hand, the activity of regular Pt nanoparticles, in which step-like defects are abundant, increases together with the size of their (111) terraces [4, 5]. These two conflicting observations preclude the straightforward use of design principles obtained from single-crystal for the design of enhanced Pt nanoparticles, and challenge our understanding of structure-sensitive effects in electrocatalysis. Therefore, the question is why do defects enhance the activity of model surfaces and decrease that of nanoparticles?

Aiming at answering this important question, in this talk I will present “coordination-activity plots” for the ORR on Pt catalysts [6]. These plots capitalize on the relationship between the geometric structure of Pt sites and their ORR activity. Such relationship is captured by generalized coordination numbers for all types of sites on model surfaces and nanoparticles of different sizes and shapes [7, 8]. “Coordination-activity plots” show that optimal Pt sites for the ORR possess the same number of first nearest neighbors as sites on Pt(111), but the number of second nearest neighbors must be larger. Such condition is found at concave sites, which are present in stepped surfaces but not in regular nanoparticles [9].

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CHARGE AND STRESS TRANSFER IN DEFORMED 2D MATERIALS

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Two-dimensional (2D) materials like graphene or transition metal dichalcogenides brandish many unique virtues, ranging from high electric or thermal conductivity via optical transparency to extreme strength or Young modulus, which are greatly enhanced compared to the same properties of the bulk progenitors [1]. On the other hand, the loss of protection provided by the neighbouring layers makes the 2D materials extremely susceptible to their environment [2]. This sensitivity can be (and often is) a hindrance in potential high-tech applications of 2D materials, but in the same time it can provide an additional boost when properly controlled and utilized. The first step, however, lies in the determination of the state of the material, especially in terms of charge carrier density and strain, both of which are known to influence crystal as well as electronic structure of the 2D material [3,4]. Raman spectroscopy is an ideal tool for such analysis, due to its non-destructive character, speed and simple operational conditions. Nevertheless, discrimination of charge and stress effects, e.g., in graphene, requires a more advanced analysis, because these two effects are superposed in the Raman spectra. In a simpler case, combining only biaxial strain and hole doping (from air molecules or dipoles in the substrate), vector analysis of the data points in the G and 2D band positions phase space suffices to extract carrier density and strain level quantitatively [5]. When other factors (uniaxial strain, both p- and n- doping, spatial inhomogeneities etc.) are present, spectral widths and intensities of the G and 2D Raman bands have to be employed [6], ideally complemented by the analysis of another Raman band like the 2D' [7], which is commonly omitted from the interpretation of the Raman spectra of graphene due to its low intensity.

Acknowledgement

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SHOULD ELECTROCHEMISTS BE AWARE OF SURFACE GASEOUS NANOBUBBLES?

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Surface gaseous nanostructures – nanobubbles and nanopancakes – frequently occupying interface of water-immersed solid surfaces represent emerging topic of potentially high impact on various fields utilizing interfacial processes. In the kinetics of electrochemical gas evolution and degassing the nanobubble is presumed to play the role of nucleation center. In biophysics and biochemistry it addresses important issues of transmembrane gas exchange, decompression illness mechanism etc.

Our work focused on mutual correlation of interfacial processes and nanomorphology of solid (electrode) surfaces utilizing atomic force microscopy in situ and in electrochemical environment, revealed clearly nanobubble interaction with solid surfaces. This interaction is exhibited, besides observed rearrangement of surface nanomorphology [1 - 3], also by influence on mass transfer processes like electrodeposition, adsorption [4] and nanoporous membrane blockade [5]. In addition, nanobubble-made imprints in polymeric matrix can be utilized for “noncontact” ex-situ identification of nanobubble presence [6][7] and alternatively, question can be raised on nanobubble as a surface nanopatterning tool.

The surface nanomorphology, namely the density of gas-filled nano-pockets present on immersed surfaces appears to affect the nanobubble appearance numbers. Both chemical hydrophobicity (due to absence of hydrophilic (e.g. oxide) groups) and physical (nanostructural) hydrophobicity of otherwise chemically hydrophilic surfaces affects the wettability of immersed surfaces and hence the nanobubble population, which, in turn, may influence charge and mass transfer efficiency of heterogeneous electrochemical processes, potential drift of gas-diffusion electrodes (GDE) in fuel cells and common solid electrodes where the gas evolution becomes an option.

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SPECTROSCOPY, CHEMISTRY AND SPECTROELECTROCHEMISTRY ON GRAPHENE

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Graphene is a new material with many prospective applications. Because graphene is 2D material, its properties are highly sensitive to the external environment. Consequently, one can dynamically tune graphene by external inputs like doping or strain. In addition graphene surface can be chemically modified, which leads to permanent change in its electronic structure.

Using Raman spectroscopy and in situ Raman spectroelectrochemistry we probe the influence of applied doping and strain on the properties of graphene monolayers and bilayers. With the help of isotope labelling we are able to address the specific behaviour of the top and the bottom layer in case of graphene bilayer. The approaches to chemical functionalization of graphene and possibilities for the reliable detection of the graphene functionalization will be also discussed.

WATER SPLITTING ON ILLUMINATED SEMICONDUCTORS – SURFACE SENSITIVITY OF THE HYDROGEN AND OXYGEN EVOLUTION ON TITANIUM DIOXIDE POLYMORPHS

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Photo-electrochemical water splitting represents one of the key processes needed for successful utilization of renewable energy sources for distributed generation, storage and use of energy.[1] The research related to the electrochemical and photo-electrochemical splitting of water is primarily motivated by electricity storage in hydrogen. The overall process itself, however, is limited by the kinetically sluggish oxygen evolution reaction (OER). Primary effort was therefore focused on a development of new oxygen evolution catalysts based on rational design approach combining the DFT screening with target synthesis. This approach turned out to be quite successful has identifying feasible new oxygen evolution catalysts based on first-row transition-metal oxides (Mn, Fe, Co, Ni) [2, 3] and perovskites [4] matching or surpassing the activity of iridium- and ruthenium oxides.

Surprisingly, the same approach has not yet be implemented for systematic development of the novel (photo)catalysts capable of direct conversion of the radiation energy into energetically useful hydrogen. The application of the rational design approach is hindered by a lack of the fundamental understanding of the electrocatalytic behavior of illuminated semiconductors. The presented paper will, therefore, focus on the hydrogen and oxygen evolution on illuminated TiO₂ (anatase) electrodes. The characteristic surface sensitivity of the catalytic behavior of anatase surfaces will be demonstrated on the nano-particulate materials dominated by {110}, {101} and {001} oriented surfaces. The photo-electrochemical data will be complemented with differential electrochemical mass spectroscopy detection of the reaction products and discussed in terms of the models of the catalytic behavior based on first principle DFT calculations.

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TITANIA AND HEMATITE PHOTOANODES FOR PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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Titania (TiO₂) and iron oxide (α -Fe₂O₃) hematite thin films have the potential applications as photoanodes for hydrogen production via photoelectrochemical water splitting. Great advantages of TiO₂ are its low price, high stability and nontoxicity. However, for practical applications, there is a huge disadvantage consisting in utilization of very small part of sunlight (4%). Iron oxide (α -Fe₂O₃) has favourable band gap (2.0–2.2 eV), which allows absorbing a substantial fraction of solar spectrum, resulting in the theoretical maximal solar-to-hydrogen (STH) conversion efficiency 15%. But there are also limitations, e. g. the non-ideal position of hematite's conduction band, which is too low for spontaneous water reduction. Therefore the aim of the present work was the comparison of TiO₂ and α -Fe₂O₃ photoanodes and the efficiency evaluation for hydrogen evolution via water splitting.

Photo-electrochemical measurements were performed in glass cell with quartz window using three-electrode arrangement in 1 M sodium hydroxide electrolyte. Pt plate was used as counter electrode and Ag/AgCl as reference electrode. Solar simulator with AM1.5G filter and irradiance 1 sun (100 mW/cm²) was used as light source. Linear voltammetry of prepared layers was measured with sweep rate 10 mV/s while periodically illuminated (5 s light/5 s dark). Amperometry at constant potential was used to determine the ageing of prepared layers under photoelectrochemical load.

Efficiency of photoelectrochemical water splitting depends on the electrochemical arrangement. For real device operated in 2-electrode arrangement (controlled potential difference between two electrodes of unknown absolute potential=BIAS), it is possible to determine real device performance as open circuit voltage, current as a function of BIAS and solar to hydrogen (STH) efficiency. Because both electrodes affect performance (photocurrent vs. BIAS) 2-electrode cell arrangement does not give information about the performance of individual electrodes. For this purpose we have to use 3-electrode arrangement and control the potential of working electrode (photoanode) with respect to the reference electrode or control the bias and measure the potential of working electrode (photoanode) and counter electrode (Pt) with respect to the reference electrode. Both experimental approaches were employed in the present work and photocurrent and hydrogen evolution rate was evaluated as a function of applied electrode potential and BIAS.

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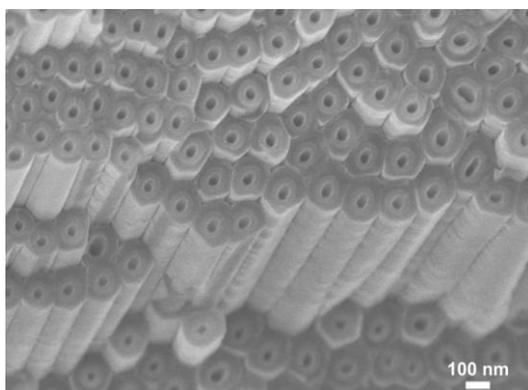
TOWARDS FUNCTIONALIZATION OF TiO₂ NANOTUBULAR LAYERS BY SECONDARY MATERIALS

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Self-organized valve oxide metal nanostructures [1-3], attracted significant attention due their potential in different applications. In particular, the TiO₂ nanotube structures received the highest attention after porous Al₂O₃ due to their inherent semiconductive nature, unique tubular architecture and chemical stability. Outstanding performance of TiO₂ nanotubes for a larger number of applications was revealed, mainly in photocatalysis [4], solar cells [5] and biomedical fields [6]. In addition, new nanodevices with remarkable possibilities could be derived due to an internal coating or filling of TiO₂ nanotube structures with secondary materials. Several routes for modification of nanotube interiors by means of electrochemical deposition, chemical deposition, sputtering and spin-coating are available [7].

This presentation will show selected results of functional applications of nanotubes achieved by various deposition means, including most recent results obtained by atomic layer deposition. This technique allows the complete and homogeneous internal coating of even very high aspect ratio TiO₂ nanotube structures [8].



SEM image of Al₂O₃ coated self-organized TiO₂ nanotubes by Atomic Layer Deposition

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STRUCTURAL AND ELECTROCHEMICAL CHARACTERISATION OF THICK POROUS BORON DOPED NANO-CRYSTALLINE DIAMOND/SiO₂ NANOFIBER COMPOSITE FABRICATED BY PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION

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Boron doped diamond has excellent electrochemical properties [1] such as a large potential window in aqueous media, a high corrosion resistance as well as low background current. However, electrode surface enlargement is required for particular applications (supercapacitors and dye sensitized solar-cells) where electrode reactivity depends on its surface.

Various top-down (i.e. etching [2, 3]) or bottom-up (i.e. coating [4, 5]) methods have been developed to enlarge the ratio of the physical surface area to the geometric electrode area, i.e. the roughness factor.

In this work, thick (up to 25 μm) porous boron doped nanocrystalline diamond/SiO₂ nanofibers composite have been fabricated in a multi steps process by conventional microwave plasma enhanced chemical vapour deposition technique. Fabricated porous boron doped diamond layers were characterized by scanning electron microscopy, micro-Raman spectroscopy, electrochemically (cyclic voltammetry, electrochemical impedance spectroscopy) in aqueous electrolyte solution and physical gas adsorption method. Electrical conductivity of porous composites was also characterized by Van der Pauw measurement technique. In this presentation, measured structural and electrochemical properties, especially the differences in determination of roughness factor of porous BDD layers using physical adsorption of gas molecules on the diamond surface (Brunauer–Emmett–Teller /BET method) and by electrochemical methods in aqueous electrolyte solution, will be presented and discussed.

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BEYOND OPTICAL DETECTION OF SPINS IN DIAMOND AND APPLICATION TO SENSORS

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The aim of the talk is to report on the current state-of-the-art developments in the photoelectrical detection schemes of NV-spin resonances. Spin properties of Nitrogen-Vacancy centres (NV⁻) are being exploited mainly using Optically Detected Magnetic Resonance (ODMR) leading to benchmark applications in the field of solid-state quantum information processing, nanoscale sensing and single spin imaging, photonics and optomechanics. Recently we have employed photoelectric detection method for the detection of NV⁻ magnetic resonances (PDMR), based on the direct electric detection of electrons promoted to the conduction band of diamond by ionization of NV[1]. This technique could make easier the integration of NV⁻ centres to electronic chips and allow independent readout of NV⁻ centres situated closer than the diffraction limit. It might also lead to high detection efficiency since every photon has the ability to generate more than one electron-hole pair (photoelectric gain mechanism). In this talk we discuss the current state-of-the-art of photoelectric detection and benchmark its potential with optical detection techniques for quantum sensing and technology applications. The progress towards magnetometers read electrically and chemical sensors will be discussed.

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ORAL PRESENTATIONS

SHAPE SELECTIVE PHOTOINDUCED ELECTROCHEMICAL BEHAVIOUR OF THIN ZnO LAYERS PREPARED BY SURFATRON

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Thin layers of ZnO were prepared by using a special modification of the plasma-enhanced chemical vapour deposition known as surfatron. This technique utilizes the principle of surface-wave discharge powered by microwave magnetron generator. Two types of substrate holder regimes (static and movable, A-type resp. B-type) were intentionally employed for preparation of two types of surface morphologies. A series of ZnO films were yielded with thicknesses ranging from 60 nm to 1500 nm. The layers were analysed by profilometry, scanning electron microscopy, X-Ray diffraction, Raman spectroscopy, UV-light adsorption and by a number of electrochemical tests. All prepared samples were crystalline and possessing different surface morphologies. It was shown that only small differences were found for these layers by characterisation methods, but there were evident differences in XRD and profilometry data.

Photoinduced electrochemical properties of ZnO/ITO electrodes in 0.1 M Na₂SO₄ solution (unbuffered at pH 5±0.05, not stirred, and no gas purging) as electrolyte were investigated in a standard three-electrode arrangement [1, 2]. The pH value of the electrolyte solution was constant during the experiments. The prepared ZnO layer was always used as the working electrode and their area was fixed at 1 cm² by using Teflon tape. It was irradiated in a Pyrex cell with light beam of the wavelength of 365±10 nm. Electrochemical interaction between the surface and the electrolyte was measured first in the dark and under irradiation of light using the cyclic voltammetry and amperometry. The role of different layers' thicknesses was also studied. It was shown in the whole potential range of CV and for the both film types the electrolyte was stable. The values of generated photocurrent were measured at potential range (0 – 1.2 V) by linear voltammetry measurement. This experiment shows the efficiency of the prepared ZnO/ITO electrode to repeatedly respond to the incident irradiation at linearly changing potential. The measured samples embodied the very sharp maximum of the reached incident photon-to-current efficiencies (IPCE) values after irradiation and spontaneous decrease in the dark phase, which was obvious for all layers of ZnO at 365 nm irradiation. The shape and crystallinity crucially influenced the films' photo-electrochemical responses. Amperometry measurements showed totally different behaviour of the films. The IPCE parameter decreased exponentially in time for A-type layers, on the other hand it increased steadily for the B-type layers. In absolute values higher IPCEs were obtained for the A-type than for the B-type layers.

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HOW CARBON NANOSTRUCTURES BASED ON GRAPHENE AND ITS OXIDES INFLUENCED THE ELECTROCHEMICAL DETECTION OF PURINE METABOLITES AND AMINO ACID TRYPTOPHAN IN CLINICAL BODY FLUID SAMPLES

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Selective and sensitive detection of small biomolecules such as purines and aromatic amino acids is urgently needed due to their important roles in human bodies. In particular, ready and accurate detection of deviations in the concentration levels of these compounds in body fluids could lead to early detection of many metabolic disorders or serious diseases [1-3]. Current medical practice relies on the biochemical, chromatographic, electrophoretic and mass spectrometric methods of monitoring these compounds in clinical samples. Although these methods provide high sensitivity in the detection of above-mentioned molecules, they suffer from several drawbacks such as requirement of a complex system, long time-consumption, or high-cost [4-6].

Therefore, many laboratories have begun to focus on the development of electrochemical methods because it soon became clear that they have many advantages, such as being easy to operate, economic, sensitive, and suitable for automation, miniaturization and field analysis [7-8]. The advent of carbon-based nanostructures such as graphene, graphene oxides, carbon nanotubes and mesoporous carbon has opened new opportunities for improvement of the sensitivity of detection of certain biomolecules in biological matrices by means of electrochemical protocols [9-10]. One of the reasons is that the nanostructured carbon-based materials have very high electrical conductivity, large surface areas, profuse interlayer structures and abounding functional groups involved, which is beneficial to the construction of novel electrochemical interfaces. Also, biocompatible carbon-based nanostructures not only facilitate bimolecular binding but also accelerate electron transfer, and thus amplify the electrochemical detection signal [9-13].

As can be seen from Figure 1, the presence of a certain type of carbon-base nanostructure (both of basal- and edge-oriented graphene sheets) on different carbon-based materials not necessarily lead to the equally huge increase in oxidation signals of studied compounds (three purine catabolites hypoxanthine, xanthine and uric acid).

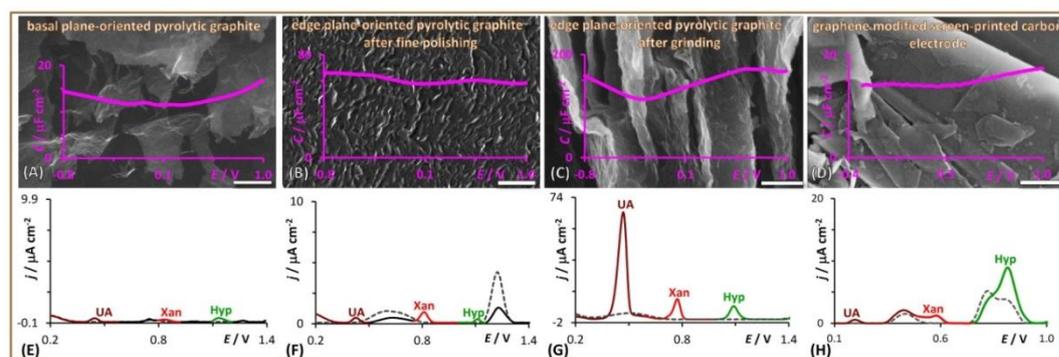


Figure 1. Top panels represent the SEM pictures and capacitance measurements (pink curves, 100 Hz) of (A) basal plane-oriented pyrolytic graphite electrode, (B) fine polished edge plane-oriented pyrolytic graphite electrode, (C) mechanically micromachined edge plane-oriented pyrolytic graphite electrode with parallel oriented graphene sheets and (D) graphene modified screen-printed graphite electrode. Bottom panels show the baseline corrected differential pulse voltamograms of an equimolar mixtures of UA + Xan + Hyp (each of 1 μM) measured at different carbon-based electrodes (E-H). Gray dashed curves in (E-H) represent the baseline corrected DPV responses of background electrolyte (0.1 M acetate buffer) at different carbon-based electrodes.

This contribution deals with the application of a few carbon nanostructures based on graphene and its oxides, which have been manufactured by mechanical micromachining and/or electrochemical exfoliation in weak acid solution, for sensitive and simultaneous electrochemical detection of purine metabolites and amino acid tryptophan in blood plasma or urine clinical samples [14]. The detection of purine metabolites includes: (i) purine metabolites that are involved in the xanthine oxidase pathway (hypoxanthine, xanthine and uric acid), (ii) methylated xanthines that are present due to intake of food and beverages and (iii) purine analogs used as therapeutics for treatment of gout (allopurinol and its metabolite oxypurinol).

Acknowledgments

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DO NANOBUBBLES EXIST IN BULK LIQUIDS? CAN WE PREPARE THEM ON DEMAND?

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According to well accepted theory based on kinetic of gas dissolving in liquids, any small gaseous bubble (μ -bubble and nanobubble) once formed in the solution, should disappear in less than few milliseconds due to a high internal pressure caused by surface tension and high curvature of these bubbles. Despite it, recently a lot of papers has been published dealing with existence of such bubbles stable for hours or even of days, though no plausible theory has been given explaining their stability.

While the existence of surface nanobubbles, i.e. nanobubbles “sitting” on solid|liquid interface, has been proved by several techniques (the surface nanobubbles can be directly observed, e.g., by AFM microscopy), the existence of stable nanobubbles in bulk is still doubtful. The problem is in the difficulty to prove the existence of gaseous nanodomains, which are mobile, cannot be isolated and imaged by conventional imaging techniques. Nevertheless, many papers have been published describing effects assigned to them.

In this contribution we want to show possible way of generating bulk nanobubbles in pure water by combination of mechanical generation of small bubbles and their simultaneous disruption by ultrasound. The proof of their existence is based mainly on (dynamic) laser light scattering (DLS). A special arrangement for sonication eliminating possible contamination of solution by nanoparticles of titanium from the ultrasonic horn has been used [1]. Such arrangement is very convenient also for sonoelectrochemical applications related to cavitation effects.

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ENHANCED PEC WATER SPLITTING EFFICIENCY OF HIGHLY TEXTURED HEMATITE PHOTOANODES

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Hydrogen production from photoelectrochemical (PEC) water splitting driven by solar power is one of the clean technologies that can be used for environmentally friendly fuel production. Iron oxide (α -Fe₂O₃) with hematite crystalline structure possesses many advantageous properties. The material's substantial light absorption, offering potential conversion of up to 17% of the sun's energy into hydrogen (band gap energy between 2.0–2.2 eV), nontoxicity, high stability in aqueous environments, ample abundance and low cost are generally superior compared to other photoanodes. [1-3]

In the present work, we attempted to tune the crystal orientation of hematite 2D thin nanocrystalline photoanodes by carefully controlling the energy of particles bombarding the substrate during a plasma assisted deposition procedure, i.e. a magnetron sputtering process. [4-6]

The highly oriented hematite films examined in this study were fabricated by DC pulse reactive magnetron sputtering of a pure iron target working as a cathode in an Ar/O₂ gas mixture. Three different pulsing regimes of deposition magnetron discharge were used: (i) high impulse power magnetron sputtering mode (HiPIMS, 0.1 kHz), (ii) pulsing sputtering mode (PS, 1 kHz), and (iii) medium frequency sputtering mode (MFS, 50 kHz). As a result of different pulsing frequencies, f_p , and duty factors of a pulsing cycle, d_u , used, various cathode pulse current densities were reached. During each deposition, the average current, I_{AV} , and, consequently, average current density, j_{AV} , were kept constant at 600 mA and 32 mA/cm², respectively.

XRD patterns of films are presented in Figure 1. It can be seen that the main variation was in the two most intense diffraction peaks corresponding to (110) and (104) reflections (in hexagonal coordinates) due to hematite, α -Fe₂O₃ (Figure 1). Only in the case of the MFS films, both these diffraction peaks occurred, suggesting the common polycrystalline hematite form. The main reflection observed in the spectrum for the PS film was from the (104) plane, whereas the desired preferential phase orientation along the (110) plane was unambiguously identified in the XRD pattern of the HiPIMS film.

Large differences in the PEC simulated water splitting performance were observed between the tested films (Figure 1). In these experiments, J - V polarization curves were measured under standard AM 1.5 G (intensity 100 mW cm⁻²) chopped light illumination. The highest photocurrent values (0.28 mA cm⁻² at 1.23 V and 0.65 mA cm⁻² at 1.55 V vs. RHE) were obtained with the HiPIMS fabricated hematite photoanodes. Since all experimental conditions were kept identical and the examined photoanodes differed principally in the preferential alignment of the crystallites, the excellent photoactivity of the HiPIMS photoanode was most likely due to the favorable conductivity of the majority

carriers (electrons) along the [110] axis (*c*-axis) perpendicularly connected to the FTO substrate. The second highly textured hematite photoanode deposited using the PS mode exhibited an almost negligible plateau photocurrent of 0.02 mA cm^{-2} at 1.23 V vs. RHE, which remained almost constant until the water oxidation dark current onset. This drastic decrease can be explained by the synergetic effect of low electron and hole mobilities within the (104) plane oriented parallel to the *c*-axis and its non-ideal oxygen dominated surface termination, which is believed to cause much higher surface recombination due to the high density of surface states acting as traps. The most cathodically shifted dark current onset corresponding to the PS photoanode can also be attributed to the surface or defect states. In between the two extremes (HiPIMS and PS films), the photoactivity of the untextured MFS films showed a photocurrent maxima of 0.14 mA cm^{-2} at 1.23 V and 0.38 mA cm^{-2} at 1.55 V vs. RHE. This result is consistent with the XRD patterns, which showed that both discussed planes were present almost equally.

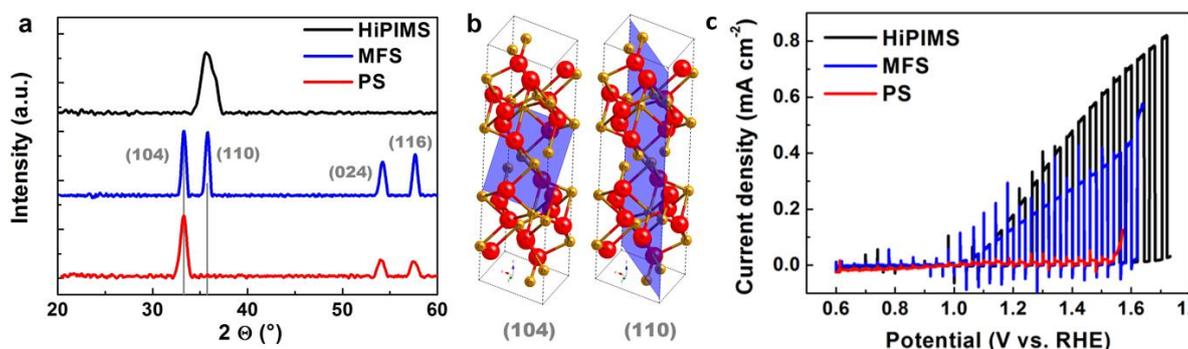


Figure 1: (a) X-ray diffraction patterns of hematite films deposited on the amorphous fused silica substrates; (b) models of the hematite crystal lattice with (104) and (110) preferentially oriented planes displayed; (c) simulated PEC water splitting activity of hematite photoanodes deposited under different energy of substrate ion bombardment. The PEC characteristics were recorded under solar light AM 1.5 simulated conditions with an intensity of 100 mW cm^{-2} , using 1 M KOH solution as the electrolyte, and with a scan rate of 1 mV s^{-1} .

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INVESTIGATION OF ELECTRON TRANSPORT THROUGH TOWER-SHAPED MOLECULAR CONDUCTORS BASED ON THE TETRAPHENYLMETHANE TRIPOD STAND

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Molecular electronic devices are considered to potentially replace currently used electronic devices based on silicon semiconductor technologies. Molecular electronic circuits inevitably require effective molecular conductors capable of transporting sufficient amount of electric charge over long distances with reasonably low attenuation. This might be secured by molecular systems showing electron hopping as the charge transport mechanism, due to its weak electric conductance-distance dependence. Such molecular systems are therefore intensively sought.

In this work, we use scanning tunnelling microscopy break junction (STM-BJ) technique to investigate the charge transport properties within two series of tower-shaped molecular conductors with variable molecular length (Figure 1).

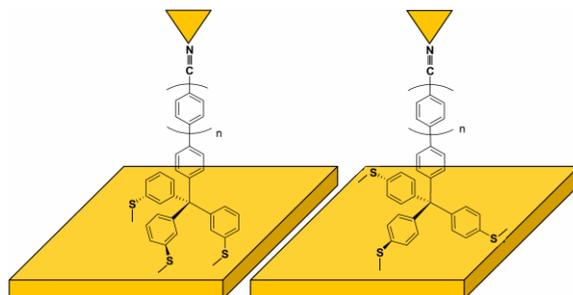


Figure 1 Depiction of molecular junctions containing *meta* (left) and *para* (right) type molecular towers inspected in this study. Number of repeating units $n = 1 - 4$.

Tetraphenylmethane moiety serves as the tower base. Three thiolate anchoring groups (located on three lower benzene rings either in the *meta* or *para* position with respect to the central sp^3 carbon atom) are employed to secure a firm electronic coupling between the molecular tower and the STM substrate. The connection to the gold STM probe is realized by the cyano group at the top of the molecular tower.

STM-BJ technique relies on a repetitive formation and breaking of molecular junctions, in which the substrate and the probe are bridged by a single molecule, allowing its electric properties to be scrutinized. The conductance of the molecular junction is measured and recorded in the course of the junction evolution, at a constant bias voltage applied. Typically, several thousand of individual molecular junctions are formed and inspected, to obtain statistically significant results. The latter are presented in the form of 1D and 2D logarithmic conductance histograms.

Figure 2 shows 1D and 2D histograms obtained for the *para* type tower with $n = 1$. The most probable molecular junction configurations manifest themselves as regions with

the highest data density. For all molecular towers inspected in this study, two molecular conductance features were observed (denoted as G_H and G_L in Figure 2). The G_H feature was attributed to early stages of the molecular junction evolution, where the bridging molecule is inclined with respect to the substrate surface (configuration not shown). The G_L feature, which shows up upon further junction elongation, is a signature of the fully extended molecular junction, in which the axis of the molecule is perpendicular to the substrate surface, as shown in Figure 1. The fully extended molecular junction appears just before the breaking event, which is detected by a steep decrease in the conductance down to the instrumental noise level of $\sim 10^{-6.5} G_0$ (Figure 2, right), where $G_0 = 77.5 \mu\text{S}$ is the conductance quantum.

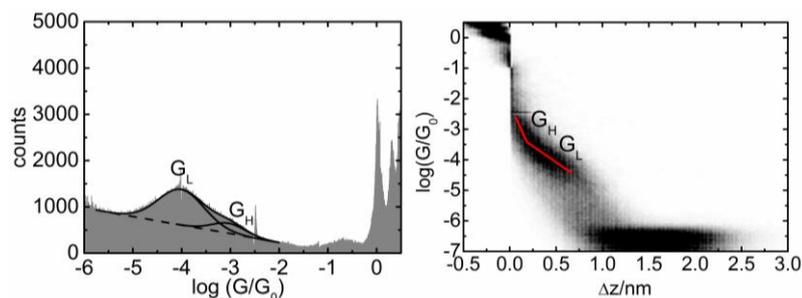


Figure 2. 1D (left) and 2D (right) conductance histograms obtained for the *para*-type molecular tower with $n = 1$. Red lines are plotted to depict G_H and G_L features.

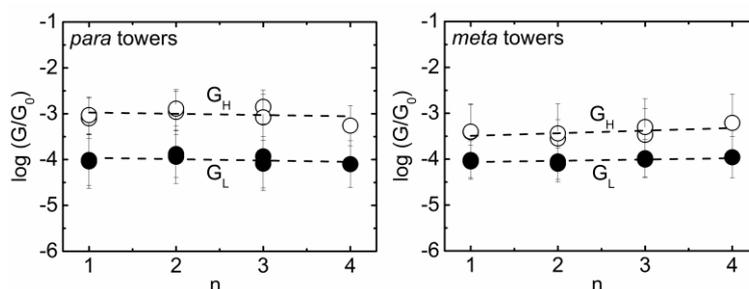


Figure 3. Length dependence of the average molecular conductance values.

The average conductance value of the G_H feature was found to be roughly a half order of magnitude higher for *para* towers compared to *meta* towers (Figure 3). This indicates that the structure of the tower base influences the charge transport in early stages of the molecular junction evolution. Thiolate anchors positioned in the *para* positions appear to facilitate the charge transport, as predicted theoretically [1]. On the other hand, the average conductance value of the G_L feature is clearly independent of the tower base structure. The charge transport through the fully extended molecular junctions is therefore most likely limited by the central sp^3 carbon atom. Importantly, average conductance values of both G_H and G_L features were found to be independent of the molecular length for both types of towers. This suggests that the charge transport is governed by the electron hopping. The inspected tripod appears to be an attractive platform for further studies leading to real molecular electronic elements capable of efficient long range electron transport.

Acknowledgements

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DIAMOND PHOTOCATHODES FOR DYE-SENSITIZED SOLAR CELLS

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The sensitization of wide band-gap semiconductors to visible light is intensively studied in the area of n-doped electrode materials, such as TiO₂, which forms a basis for the dye-sensitized solar cell (DSC). The most successful material for an active photocathode is p-doped NiO, but the highest efficiency obtained so far for the p-DSC is only 1.3%. [1,2] The final goal of these efforts is obviously a tandem device (p,n-DSC) in which both electrodes are the photoactive semiconductors. The tandem cells are attractive due to their enhanced voltage, which is not controlled by the redox potential of the mediator anymore, [3] but these cells cannot rival the efficiencies of the optimized n-DSCs at the moment.

Among the alternative photocathode materials, the B-doped nanocrystalline diamond (BDD) can be considered a promising replacement of p-NiO. Diamond films made by CVD are attractive due to their excellent chemical and electrochemical stability, optical transparency and favorable electrical properties. BDD is better optically transparent than p-NiO, approaching the optical quality of indium-tin oxide (ITO) at certain levels of doping. [4,5]

The donor- π -bridge-acceptor dye, 4-(bis-{4-[5-(2,2-dicyano-vinyl)-thiophene-2-yl]-phenyl}-amino)-benzoic acid (coded P1) is one of the most efficient chromophores which is frequently used for the sensitization of p-NiO and of some other p-type semiconductors. [7] Non-covalent anchoring of P1 to diamond was performed by two different methods. The first one was a two-step procedure, polyethyleneimine (PEI) was adsorbed on H-terminated BDD, and subsequently modified with P1 and the second novel strategy was direct covalent anchoring of P1 dye to the surface of H-terminated B-doped diamond electrode. The second procedure leads to improved efficiency, nevertheless, illumination of the P1 dye by 1-sun light causes also some degradation.

A light-harvesting efficiency of a monolayer of dye molecules on a flat surface of B-doped nanocrystalline diamond is inherently small. The growth of nano-textured mesoporous diamond films was attempted by templating with SiO₂ fibers and SiO₂ spheres. So called nanodiamond foam was grown by using SiO₂ spheres (500 nm in diameter) as templates, on which a thin BDD layer was deposited by standard chemical vapour deposition growth. The template was subsequently etched away by HF solution, leaving hollow spheres of diamond which replicated the SiO₂ template.

To directly compare flat diamond films and diamond foams, we have functionalized the diamond foams with the same dyes ((E)-2-{4-[2-(6-bromo-4,4-diethyl-4Hcyclopenta[1,2-b:5,4-b']dithiophen-2-yl)vinyl]-3-cyano-5,5-dimethylfuran-2(5H)-ylidene}malononitrile (coded CPDT-Fur) and (Z)-2-{5-[(5'-bromo-[2,2'-bithiophen]-5-yl)methylene]-4-oxo-2-thioxothiazolidin-3-yl} acetic acid (coded BT-Rho)) as applied in our previous work on flat BDD films. [6] These molecules were anchored by the Suzuki coupling protocol through a phenyl linker, which was attached to the originally H-terminated diamond surface by diazonium electrografting.

The prepared materials were tested as electrodes in the dark and upon illumination in an aqueous electrolyte solution with methyl viologen acting as a reversible electron acceptor. Reference experiments were carried out with standard flat BDD films, too.

Cathodic photocurrent densities for a fresh foam electrode sensitized with both CPDT-Fur and BT-Rho illuminated by white light (20 mW/cm²) are approximately 3-times larger than those on flat diamond, which is attributed to the enhanced surface area of the foam electrodes.

Acknowledgment

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EXPANDED BRANCHED PYRIDINIUM DERIVATIVES: STRUCTURE – SINGLE MOLECULE CONDUCTANCE RELATIONSHIP

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The continuing trend of miniaturization of the electronic components is in great agreement with the Moor's law [1]. Nevertheless, the limit of this prognosis is approaching because of the minimal achievable dimensions of the components. One of the possible solutions is the replacement of the electronic parts by specialized molecules [2]. Among the promising molecules rank the extended and expanded pyridinium derivatives [3].

The expanded branched pyridinium molecules studied here differ in their reduction mechanism [4, 5]. The compounds from the first group are reduced in two separated one-electron steps. The molecules from this class allow only minimal structural change on the pyridinium moiety upon the electron transfer process. On the other hand, the first electron received by the molecules in the second class causes strong structural change which makes the reduction by the second electron much easier. This causes the potential compression and just one two-electron signal is measured.

The unusual electrochemical properties of expanded branched pyridinium derivatives led us to study the relationship of their chemical structure and the single-molecule conductance in metal-molecule-metal junction arrangement. The influence of the structure, respectively of the electrochemical properties, on the conductance could help to design new molecular wires applicable to molecular electronics.

Three representatives of expanded branched pyridinium molecules (see Fig. 1) were synthesized for this purpose.

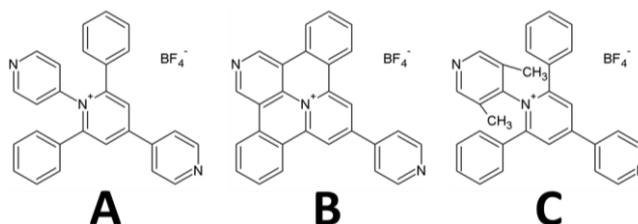


Fig. 1: Structure of studied compounds.

The electrochemical reduction of the compounds were studied by voltammetric methods on hanging mercury drop electrode and platinum electrode in dimethyl sulfoxide and acetonitrile solvents. Compound A provides just one two-electron signal during its reduction. It is caused by the change of the structure induced by the first electron, which promotes the reduction of the molecule by the second electron. The structures of

compounds **B** and **C** are locked against the structural changes and for this reason two separated one-electron signals are visible.

The single-molecule conductance measurements were done by the Scanning Tunneling Microscopy Break Junction (STM-BJ) technique. The aim is the formation of the molecular bridge between two gold electrodes, which are connected to a source of the constant voltage. The connection between the gold electrodes is allowed by the specific interaction of the terminal nitrogen atoms of the compounds with gold. All of the studied molecules provided two values of single-molecule conductance. This is typical for molecules terminated by pyridinium groups [6]. Higher values of conductance were obtained for the compounds **B** and **C**. The highest value was measured for compound **B**, it was more than twice as high as the value for the compound **C**. The difference of the values measured for compounds **C** and **A** was not so significant.

Acknowledgment

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HYPPOCHLORITE OXIDATION ON NANOCRYSTALLINE RuO₂ – UNWANTED PARASITE OR SOLUTION FOR THE PLANET?

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Hypochlorite oxidation represents one of the key parasitic reactions degrading the efficiency as well as safety of the chlorate process. The oxidation of hypochlorite has been known to yield oxygen and chlorate(s) and to be affected by both electrode material as well as pH. A detailed mechanism of the process however, remains unknown, despite the attention paid to the process during the last 100 years. This paper will present results of a systematic hypochlorite oxidation study employing a combination of voltammetry with on-line mass spectrometric detection of the reaction products on nanocrystalline RuO₂ based electrodes.

Anodic oxidation of the hypochlorite anion triggers catalytic water splitting in alkaline solutions. Hypochlorite oxidation on polycrystalline platinum yields ClO· radicals which initiate a radical assisted water splitting yielding oxygen, hydrogen peroxide and protons. The efficiency of the oxygen production corresponds to ca. 2 electrons per molecule of the produced oxygen and is controlled primarily by the hypochlorite concentration and pH. The pH of the electrolyte solution primarily controls the protonation of the hypochlorite. Additionally, the course of the hypochlorite oxidation is also affected by the selectivity of the electrode surface towards chlorine evolution which is controlled by the local surface structure (and chemical composition) as well by the pH of the electrolyte solution.

A QUANTUM CHEMICAL STUDY OF THE ETHYLENE OXIDATION AT NANOSTRUCTURED GOLD AND PLATINUM ELECTRODES

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Density functional theory (DFT) calculations are used to investigate the catalytic reaction mechanism of ethylene with adsorbed oxygen on platinum cluster Pt₂₁ or on gold clusters Au₂₂. Gibbs free energy based analysis of the ethylene oxidation on Pt₂₁ or Au₂₂ cluster was employed to interpret the experimental data. DFT calculations encourage experimental findings and indicate possible reaction pathways of catalytic reaction. DFT calculations do not show the different reactivity on individual types of surfaces. The effect of spin multiplicity and influence of external electric field and solvent effect were investigated by our calculations.[1]

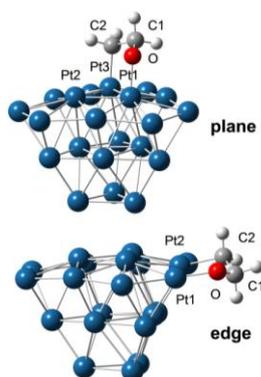


Figure 1. DFT optimized structures of oxametallacycle intermediates interacting with Pt₂₁ clusters

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OXYGEN REDUCTION ON Pt CATALYSTS IN H₃PO₄ ELECTROLYTE AT ELEVATED TEMPERATURE

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Fuel cells with proton exchange membrane, a vital part of Hydrogen Economy, are widely recognized as highly efficient devices for conversion of chemical energy of H₂ and O₂ to the electricity. High temperature fuel cell with proton-exchange membrane (HT PEM FC), a modification of the previous technology, came to prominence in recent years. Due to its operating temperature of 120–200 °C rate of electrochemical reactions is increased and Pt catalyst is thus less prone to the poisoning by CO. Higher operation temperature requires use of polybenzimidazole-type polymers doped with H₃PO₄ as a proton conducting membrane since perfluorosulfonated-type membranes undergo drying at temperatures above 100 °C under atmospheric pressure and thus lose conductivity. Main drawback of HT PEM FC lies in the presence of H₃PO₄ in the membrane. Degradation processes are greatly enhanced by combination of H₃PO₄ and high temperature. Significantly pronounced degradation process represents growth of Pt nanoparticles caused by either agglomeration and sintering or Ostwald ripening of catalyst.

To counter the degradation processes in HT PEM FC, new Pt-based catalysts are being developed. Research is focused on investigation of highly durable supports for Pt nanoparticles. An ideal support should be cheap, suitable for modification by Pt, easily dispersible and resistant to oxidation under harsh conditions on fuel cell cathode. Several materials match such description, between others carbon nanowires and nanotubes or carbides of metals and semimetals. For catalyst characterization purposes electrochemical methods enable direct investigation of reactions by means of e.g. impedance spectroscopy or voltammetry. To perform electrochemical measurement catalyst is usually immobilized on the surface of electrochemically inactive and electrically well conductive material. Immobilization can be performed on gas-diffusion electrode or rotating-disk electrode using polymeric binder. Use of precise metal capillary stuffed by catalyst is also an option. Catalyst immobilization on rotating-disk electrode, so called thin-film method, is the most versatile one of listed procedures. It is useful not only for study of reaction kinetics but also for determination of transport parameters of electroactive species in electrolyte.

Rate of electrochemical reactions as well as mass transport processes determine performance of HT PEM FC. Hydrogen oxidation on anode is a reaction with rather fast kinetics. On the other hand, oxygen reduction reaction (ORR) on cathode in the presence of concentrated H₃PO₄ has very sluggish kinetics. Thus, ORR is main factor limiting HT PEM FC performance. Despite rapid development in the area of HT PEM FC catalysts, no adequate method based on thin-film was introduced for ORR investigation related to HT PEM FC operating conditions. Determination of catalytic activity is ordinarily performed in diluted aqueous solutions at ambient temperature, i.e. conditions hardly

corresponding to the environment of HT PEM FC. This is caused by limited number of usable polymeric binders, thin-film mechanical stability issues and material limitations of commercial rotating-disk electrodes.

The aim of this work was to modify thin-film method on rotating-disk electrode to be applicable in 100% H₃PO₄ at 160 °C for determination of Pt/C catalysts ORR activity. Instead of commercial rotating-disk a high-temperature glassy carbon rod was used as the electrode. To evaluate the effect of cylindrical insulation around disk a series of tests was performed. Impact of ink preparation and Pt loading on electrochemically-active surface area and ORR activity was evaluated. ORR was successfully studied by the modified thin-film method using glassy carbon rod. O₂ diffusion coefficients in the electrolyte solution and the binder layer were determined along with Tafel kinetic constants of ORR. Activity of Pt-based catalysts with supports including carbon nanowires, nanotubes and SiC-TiC will be compared and discussed.

Acknowledgements

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FUNCTIONALIZED GRAPHENE-ENHANCED RAMAN SCATTERING

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A concept of graphene-enhanced Raman scattering (GERS) was proposed and demonstrated in 2010 [1]. It was observed and demonstrated that molecules even in very low concentrations exhibit a reasonable Raman signal when placed on a graphene layer. Furthermore, the photoluminescence quenching of molecules on graphene was observed [2], which helped to make the GERS effect observable. Recently, GERS has been suggested for applications in chemical and biological sensing devices [3]. The enhancement originates from electronic interactions between graphene and the molecules [4]. Therefore, shifting graphene's Fermi level may lead to extension of the range of detectable molecules by GERS-based chemical sensor.

In our work, we used variously functionalized graphene (fluorinated, thiophenol functionalized, diazonium functionalized and pristine) as underlying layers for Rhodamine 6G (R6G) molecules. The Raman signal from the R6G molecules was observed for all the investigated functionalizations of graphene, while on bare Si/SiO₂ substrate the R6G molecules did not show any measurable signal. We found that the functionalization induces changes in the doping of graphene. Generally, the enhancement was found to be increasing with increasing phonon energy of the R6G molecule and with electronic doping of graphene. The highest enhancement was detected for diazonium functionalized graphene sample.

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ELECTROCHEMICAL CHARACTERIZATION OF P- AND N-TYPE DOPED DIAMOND ELECTRODES

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The large band-gap 5.5 eV of undoped diamond causes, that diamond is normally electrically insulating. However, due to its favorable properties, which combine chemical resistance, optical transparency, thermal conductivity, high bio inertness and electrochemical properties, it is very useful to prepare diamond as a semiconductor or material having a metallic conductivity. Depending on the incorporated element into the diamond lattice we can get diamond with *p*-type (boron) or *n*-type (phosphorus) conductivity. Such conductive diamond could be used in electronic applications, for application in *p*-type dye-sensitized solar cells or in bioelectrochemistry. In situ Raman spectroelectrochemistry is a technique combining Raman spectroscopy and electrochemistry, which allows monitoring of structural and electronic (shift of Fermi level) changes of an electrode material as a results of different potentials applied. The electrochemical measurements have been performed in aqueous electrolyte solution (0.5M H₂SO₄, pH 0.6) in the potential range of -1.5 to 1.5 V vs. Ag/AgCl. As a working electrode were used nanocrystalline boron-doped diamond (B-NCD; *p*-type) and phosphorus-doped diamond (P-NCD; *n*-type) thin films grown by MPECVD. The prepared diamond films were doped with various boron concentrations of 500–8000 ppm (B/C ratio in the gas phase) and with phosphorus concentration of 10 000 ppm (P/C ratio in the gas phase). In the case of B-NCD, it was found that the modes belonging to boron incorporated into the diamond lattice (at 463 and 1220 cm⁻¹) and sp³ carbon (at 1305 cm⁻¹) exhibited no changes with the applied potential neither in anodic nor cathodic directions. This finding indicates a high stability of the diamond lattice with substitutionally incorporated boron. Conversely, the modes belonging to sp² carbonaceous phases (D, G and D' band) change their intensities; in cathodic direction increases, while in anodic direction decreases [1]. In situ Raman spectroelectrochemistry of P-NCD layers has shown the same trend (as for B-NCD) in the intensity changes of peaks corresponding to sp³ and sp² carbonaceous phases with applied potential [2]. Morphology studies (ex situ) and electrochemical measurements (cyclic voltammetry, electrochemical impedance spectroscopy) have been also performed to provide a complete picture of the prepared B-NCD and P-NCD films [2, 3].

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Prof. Jaroslav Heyrovský (20. 12. 1890 – 27. 3. 1967)

Academician Jaroslav Heyrovský is considered to be the founder (1922) of a method (polarography) that enables the fast and extremely exact determination of metals and their concentrations in solutions.

In 1924 Heyrovský, together with his Japanese disciple Masuzo Shikata, designed and built an automatic device which he named a polarograph. After World War II, the method of polarography, which was employed in science, medicine and a range of industries, achieved a massive expansion.

In 1950, J. Heyrovský founded the Institute of Polarography that was attached to the Academy of Sciences in Prague.

Heyrovský is the only Czech scientist to be awarded the Nobel Prize for chemistry (10.12.1959) in recognition of his invention of polarography, pioneering achievement and the development of polarography.

The tradition of Heyrovský Discussion was started in 1967. The Heyrovský Discussion took place always in one of the conference centers of the Czech Academy. Originally, the Discussions were held at the Liblice castle, later in castle Bechyně and recently it has taken place at the renaissance castle Třešť in southeastern Bohemia, in an attractive, peaceful locality rich in historical monuments and of beautiful natural scenery.



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