

44th Heyrovský Discussion

Nanostructures on Electrodes

Book of Abstracts



26. June – 30. June 2011

The 44th Heyrovský Discussion 2011 was held at the Conference centre in chateau Třešť in town Třešť in the Czech Republic, from 26. June to 30 June 2011.

Sponsor



44th Heyrovský Discussion

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Nanostructures on Electrodes

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Organizers

Ladislav Kavan and Pavel Janda

26. June – 30. June 2011

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PROGRAMME

Sunday, June 26th			
10:00	Registration in the entrance hall of the J. Heyrovský Institute, possibility to leave the luggage and walk in the town		
15:00	Departure of a special bus from the J. Heyrovský Institute (Dolejškova 3, Prague 8 – Kobylisy)		
18:00	Arrival, registration at the Castle Třešť		
19:30	Welcome apéritif		
20:00	Dinner		
Monday, June 27th			
from			
7:00	Breakfast		
8:30	Morning session:		
	Opening of the Discussion		
8:40	Nanoparticle on electrode 1		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
8:40	Ludvík	Wandlowski	Charge transport with single molecules and clusters - An electrochemical approach
9:40-10:20		Mészáros	Dependence of flicker noise on the surface structure of microelectrodes
		Krtíl	Surface segregation of the Au ₄ Pd nanoparticulate alloys in electrocatalytic reactions
10:20	Coffee break		
10:50	Nanoparticles on electrodes 2		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
10:50-12:10	Wandlowski	Heyrovský	Gold nanoparticles catalyze hydrogen evolution on mercury electrode
		Vlčková	Oxidized and reduced adsorption sites on AG nanoparticle surfaces
		Kolivoška	Self-organized structures of methylated- β -cyclodextrin on mercury and Au(111) electrode
		Petrikyn	Local structure and its effect on electrocatalytic behaviour of nanocrystalline RuO ₂ based materials
12:30	Lunch		
14:30	Afternoon session:		
	Nanostructure on electrodes		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
14:30-15:50	Michl	Sokolová	Growth of adsorption layer of benfluralin on the surface
		Hromadová	Electron dopable molecular wires based on the extended viologens
		Janda	Nanobubbles at solid–liquid interface
		Paleček	Thiol nanolayers at mercury and amalgam electrodes. Chronopotentiometric detection of changes in protein structures at picomole level
15:50	Coffee break		

Monday, June 27th			
16:10	Ti nanostructures		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
16:10	Frackowiak	Schmuki	TiO₂ nanotubes and other self organized anodic structures: Formation and applications
17:10- 17:50		Sadkowski	Reassessment of the Kramers-Kronig relations in the context of the stability of the titanium electrode
		Pospíšil	Extended viologens: Molecular wires as a source of oscillations
18:00	Concert of Chamber music		
19:00	Dinner		

Tuesday, June 28th			
from 7:00	Breakfast		
9:00	Morning session:		
	Carbon Section		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:00	Dunsch	Frackowiak	Nanostructured carbons for supercapacitor application
10:00- 10:40		Kulesza	Advanced functional materials for electrochemical science and technology: network films of carbon and noble metal nanostructures modified with inorganic molecules
		Randriamahazaka	Performance of bucky-gel actuators based on single-walled carbon nanotubes and ionic liquids
10:40	Coffee break		
11:10	Graphene Section		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
11:10- 12:10	Pospíšil	Fic	Graphenes for electrochemical applications
		Kalbáč	Spectroelectrochemistry of graphene and graphene layers
		Frank	Mechanical properties of graphene – a prerequisite for flexible transparent electrodes
12:15	Lunch		
14:00	Excursion by bus		
19:00	Open air party, beer, soft drinks		

Wednesday, June 29th			
from 7:00	Breakfast		
9:00	Morning session:		
	Electrochemical conversion and storage 1		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
9:00- 10:00	Vlčková	Graetzel	Light energy harvesting and charge carrier collection in mesoscopic solar energy conversion systems
10:00- 10:40		Procházka	Three dimensional construction of electrodes- open door to high capacity lithium batteries
		Vala	Diketo-pyrrolo-pyrroles for organic electronics
10:40	Coffee break		
11:10	Electrochemical conversion and storage 2		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
11:10- 12:10	Graetzel	Michl	Exploring paths toward more efficient solar cells.
12:30	Lunch		
14:30	Afternoon session:		
	Fullerenes		
<i>Time</i>	<i>Chairman</i>	<i>Speaker</i>	<i>Title of presentation</i>
14:30- 15:30	Janda	Dunsch	Endohedral electrochemistry: Fullerenes at electrodes
15:30- 15:50		Popov	Molecular and spin dynamics in pristine and charged endohedral metallofullerenes
15:50	Coffee break		
16:20- 17:30	POSTER SECTION		
19:00	Farewell dinner		

Thursday, June 30th	
from 7:00	Breakfast
9:00	Departure to Prague
12:00	Expected arrival to the Institute
12:45	Expected arrival to the Prague Airport
POSTERS SHOULD BE ON DURING THE WHOLE MEETING IN THE FOYER OF THE CONFERENCE HALL	
INTERNET AVAILABLE DURING THE WHOLE MEETING (WIFI or CONNECTION)	

ORALLY PRESENTATIONS

ENDOEDRAL ELECTROCHEMISTRY: FULLERENES AT ELECTRODES

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In endohedral metallofullerenes (EMF), the carbon cage plays a stabilizing role – that is, most of the clusters found within the EMFs are not stable without the surrounding fullerene cage. Manipulation and tuning of the valence states of thus stabilized endohedral species by electrochemical charge transfer is an interesting and promising task resulting in new developments of molecular electrochemistry. Up to now, there are several EMFs for which an endohedral redox activity has been convincingly proved by both experimental and theoretical studies. Endohedral redox activity was discovered for selected cluster fullerenes. Their number is continuously increasing with the developments in EMF synthesis and fulfillment of more dedicated (spectroelectrochemical) studies of their properties. In this contribution, the state-of-the-art in the emerging field of endohedral electrochemistry is reviewed. Representative examples of EMFs are given which exhibit endohedral electrochemical activity. The role of ESR spectroelectrochemistry in the experimental determination of new redox states accompanying endohedral redox reactions is discussed. Endohedral redox activity also raises fundamental question on the physics of the electron transfer through the carbon cage. Such phenomena as spin-charge separation and spin flow already discovered for EMFs require a detailed analysis. Thus, the matter of reversible charge storage in endohedral fullerenes raises questions of fundamental importance.

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GRAPHENES FOR ELECTROCHEMICAL APPLICATIONS

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Graphene is recently one of the most known forms of carbon. It can be defined as a flat monolayer of carbon atoms in crystal lattice, tightly packed into a two-dimensional (2D) “honeycomb” structure. If to consider its physical properties, one can conclude that graphene is completely different than the other forms of carbon –is not only the thinnest ever but also the strongest one. This unique structure causes unusual properties, e.g. graphene is found to have excellent electronic transport properties. These properties hold a great promise for applications in field like energy storage. In particular, these materials have superior electrical conductivities better than typical graphitic carbon, relatively high surface area, wide chemical tolerance and a broad electrochemical window which would be very advantageous for application in energy technologies.

To make a general insight for these materials, we have performed several electrochemical investigations of various graphene materials.

The first material, obtained by chemical reduction of graphite oxide was investigated as electrode materials for supercapacitors by galvanostatic charging/discharging in current density range 0.2–50 A g⁻¹, cyclic voltammetry (1–200 mV s⁻¹) and electrochemical impedance spectroscopy in frequency range 100 kHz – 1 mHz. The capacitance obtained for this material was about 140 F g⁻¹ at 1 A g⁻¹, with good charge propagation, small leakage current and self-discharge. Cyclability of the supercapacitor working with graphene-based electrodes is acceptable, showing 18% capacitance loss after 5000 cycles.

On the other hand, the capacity of Li-ion anode built from this material was about 522 mAh g⁻¹ in classic organic electrolyte, however, the irreversible loss of charge in this material after first cycle of discharge was high (about 22%). Cyclability data of such anodes have shown 14% capacity loss after 50 cycles.

Hydrogen storage by water reduction and *in situ nascendi* adsorption of H ad-atoms has been determined by galvanostatic method giving capacity of about 272 mAh g⁻¹ which corresponds to 1 wt% of hydrogen in graphene electrode. Observations made with cyclic voltammetry at different scan rates (1–10 mV s⁻¹) confirm such results. Additionally, Galvanostatic Intermittent Titration Technique (GITT) suggests that hydrogen in graphenes is rather weakly bonded and can be successfully applied for electrodes operating reversibly, e.g. in batteries. Similar results were obtained for graphene materials obtained by different methods (e.g. by electrochemical exfoliation of graphitic electrodes with ionic liquid assistance).

As graphenes are highly conducting mesoporous materials, they also perfectly serve as electrode materials for novel generation of electrochemical capacitors, operating in conjugated redox couple solutions as electrolyte, preserving high capacitance and excellent charge propagation even at current density of 10 A g⁻¹.

All electrochemical results have been correlated with physicochemical properties of graphene materials.

Acknowledgement

This work was financially supported by the Foundation for Polish Science, grant No. Ventures/2010-6/2 and the Ministry of Science and Higher Education, grant No. IC-31 DS 226/2011.

NANOSTRUCTURED CARBONS FOR SUPERCAPACITOR APPLICATIONELZBIETA FRACKOWIAK*

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Supercapacitor is an attractive energy source able to accumulate and/or supply a peak power in a short time. Performance of electrochemical capacitor is based on electrostatic attraction of charges in the electric double layer. Activated carbons are the most often used electrode materials. However, nanostructured carbons for instance nanotubes play a crucial role for improvement of capacitor performance.

Carbon nanotubes (CNTs) can serve as a three-dimensional support of materials with pseudocapacitive properties, e.g., electrically conducting polymers (PANI, PPy, PEDOT) or transition metal compounds (oxides, nitrides). CNTs play a perfect conducting role in these composites. Additionally due to the high resiliency of CNT additive, the supercapacitor electrodes can be charged/discharged many cycles without mechanical degradation.

The exceptional conducting and mechanical properties of multiwalled carbon nanotubes can also be used for preparation of unique carbon/carbon composites with a variable texture and nitrogen/oxygen content. CNTs can serve as a frame for carbon obtained from different polymeric precursors. In this case, the nanotubes skeleton is very profitable to prevent shrinkage during the carbonization process and consequently an interesting CNT/carbon composite is obtained for supercapacitor application. Especially attractive material is a carbon/CNT composite rich in heteroatoms. It is well known that carbons enriched in nitrogen and/or oxygen, even with a moderate surface area, can supply high capacitance values because of quick faradaic reactions. The beneficial effect of nitrogen in the composite with an incorporated nanotubular backbone has been clearly demonstrated when e.g. melamine was the carbon precursor rich in nitrogen. Nitrogen presence has a useful effect on the capacitance values, as well as for good charge propagation at drastic current loads. However, an excess of nitrogen (presumably over 15%) can definitively aggravate the conducting properties, and in turn, the capacitance characteristics and supercapacitor cyclability. The forms of nitrogen as well as oxygen functionalities present in the carbon network are especially important. They can affect differently negative and positive electrode.

Carbon nanotubes can be used as an additive in the form of entangled network but also aligned CNT array could be directly grown on various metallic substrates using chemical vapour deposition. The lack of binder and percolating agent gives a higher available surface area whereas mesopores are adapted for an efficient ion transport indispensable for quick faradaic reactions. Hence, such array serves as an excellent support for pseudocapacitive materials (Fig.1). A great improvement has been obtained in both electrolytes (aqueous and organic). A lot of research has been focused on the development of surface area of oxide deposited on nanotubes because the higher their surface area, the higher the capacitance. Metal oxides can be deposited in the various forms such as: compact layers, dendritic clusters, nanocrystals, nanobelts, nanoneedles, nanotubes and more developed morphologies. An interesting hierarchically porous flower-like MnO₂ nanoparticles electrodeposited on multiwalled carbon nanotubes, even with the moderate specific surface, are at the origin of outstanding performance of composite with capacitance of 100 F g⁻¹ at 77A g⁻¹ current load.

Additionally, the high density of this composite ($1.5 \text{ cm}^3 \text{ g}^{-1}$) allow a high volumetric capacitance of 305 F cm^{-3} to be reached. The further development of specific surface area in the form of flake-like MnO_2 can be obtained with even better capacitance performance. Metal oxide/carbon nanotube array composites can be produced also by sputtering deposition and colloidal methods. Taking into account that conductivity of nanotubes plays so essential role in electrochemical applications, it is noteworthy to mention that aligned carbon nanotubes have better conducting properties than entangled ones. One order higher conductivity of aligned material has been proved.

It is well known that pseudocapacitance reactions are often connected with volumetric changes of electrode material, the beneficial effect especially during cycling can be reached from aligned or stretchable CNTs matrices. It is noteworthy that the favourable effect of nanotubes is more pronounced if composite is prepared directly from CNTs and pseudocapacitive material than from the mixture of both components.

Currently, some novel investigations have been carried out with the ternary composites based on nanotubes, metal oxides and conducting polymers. Specific capacitance of such composite electrode, e.g., PEDOT/CNTs/ MnO_2 can reach over 400 F g^{-1} with a good charge/discharge rate, satisfactory charge retention and cycling stability. This combination takes advantage of both pseudocapacitive materials being at the origin of new generation of supercapacitor.

Among novel forms of carbon (onions, nanohorns, graphene etc.) it seems that graphene could be a perspective and concurrent material to carbon nanotubes because of moderately low cost and a perfect conductivity strongly affected by the preparation procedure. Graphene material has already been applied for capacitor application alone or as hybrid material with nanotubes showing exceptional charge propagation.

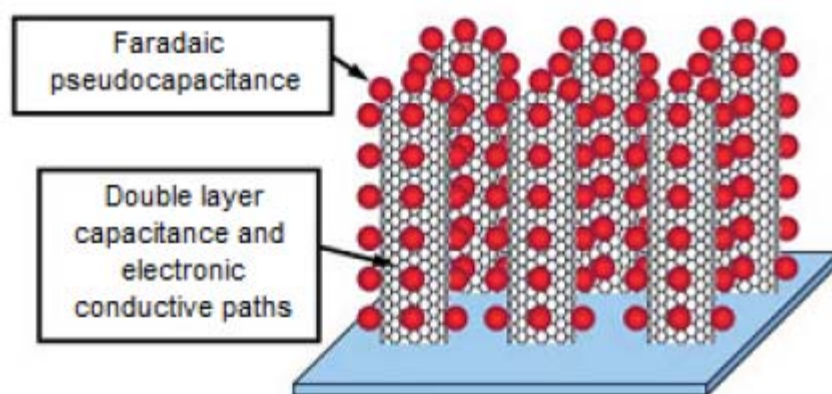


Figure 1.: A scheme of microstructure and capacitance properties of oxide-modified vertically aligned carbon nanotubes [from *W.D. Zhang et al. J. Mater. Chem. 20, 2010, 6383*].

MECHANICAL PROPERTIES OF GRAPHENE – A PREREQUISITE FOR FLEXIBLE TRANSPARENT ELECTRODES

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The presented work summarizes various aspects of uniaxial deformation in single- and bilayer graphene studied by means of Raman spectroscopy. Graphene flakes were subjected to cyclic uniaxial loading (tension - compression) using the cantilever beam technique [1,2,3]. The evolution of the Raman single-resonance (G) and double-resonance (2D, G*) bands is monitored at strain levels < 1%. Position of all bands redshifts under tension and blueshifts under compression. The G band splitting caused by symmetry lowering is observed in both directions as well and the sub-bands' intensities are used to calculate the crystal lattice orientation of the measured graphene flakes with respect to the strain axis [2]. The 2D band nature and splitting, even in the unstrained flakes, when excited by 785 nm (1.58 eV) laser line is explained and accompanied by theoretical predictions [3]. As will be shown, the flake geometry and pre-strain strongly influence the deformation behavior of the individual flakes, which is then reflected in the Raman shift rates and slopes. And importantly, differences between experiments using flakes firmly fixed in the substrate or simply laid on its surface document the slipping and non-uniform stress transfer in various stages of the loading cycles. First experiments on CVD (chemical vapor deposition) graphene show results highly relevant for its use as flexible transparent electrodes.

Acknowledgments

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LIGHT ENERGY HARVESTING AND CHARGE CARRIER COLLECTION IN MESOSCOPIC SOLAR ENERGY CONVERSION SYSTEMSMICHAEL GRAETZEL**Laboratory of Photonics and Interfaces, Ecole Polytechnique Fédérale de Lausanne, Station 6, LPI EPFL, CH-1015, Lausanne, Switzerland*

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The performance of solar energy conversion devices employing mesoscopic photoelectrodes depends critically on the nanostructure. This is evident for the dye sensitized solar cell (DSC) where charge percolation through the TiO₂ to the transparent conductive (TCO) electrodes takes milliseconds. Slow charge extraction increases chances of electron-hole recombination at the mesoporous TiO₂ - electrolyte interface, and limits DSCs to be used with only a handful of electrolytes that offer low recombination rates. These limitations can be overcome with advanced nanostructuring techniques the design of new sensitizers and new electrolytes. Here we describe our latest advances in optimizing the photon harvesting and the charge transport in these mesoscopic energy conversion systems which have reached power conversion efficiencies (PCE) over 12 percent under AM 1.5 standard reporting conditions. For the last two decades, only the triiodide/iodide redox couple has attained PCEs over 10%. A particularly exciting advance has been made by combining Co(II/III) complexes with organic donor -acceptor dyes. These systems have attained already PCEs over 10% and the recent achievement of strikingly high open circuit voltages close to 1.1 V forebodes well for realizing DSC with new record performance in the near future.

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GOLD NANOPARTICLES CATALYZE HYDROGEN EVOLUTION ON MERCURY ELECTRODE

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When cyclic voltammogram with a hanging mercury drop electrode (HMDE) in a dilute aqueous solution of chloroauric acid is recorded from 0 V vs SCE to -1.9 V and back, then at its positive end appears a prominent maximum of cathodic current (Fig.1). The maximum appears when the potential of negative scan inversion is at least -1.6 V; when this value is made more negative, the maximum increases and shifts in negative direction. This indicates that the occurrence of the maximum is connected with products of processes taking place on the mercury electrode at negative potentials. That is confirmed by single-sweep linear voltammetry with HMDE polarized from negative to positive potentials: if the potential scanning is started with increasing delay after closing the electrolytic circuit, i.e., with increasing amount of the electrolytic products formed at the initial negative potential, the maximum increases, shifts to negative potentials and, moreover, the slope of the charging current part of the curve decreases (Fig.2). The latter effect is typical for adsorption of reaction products at the electrode surface. The dependence of the maximum on the rate of voltage scan indicates that the species producing the positive cathodic current maximum is short-lived: with scanning rate of 20 mV per second and slower the maximum does not appear, with faster rates the maximum appears, increases and shifts to negative potentials. The occurrence of the maximum is limited to a narrow pH range of the electrolysed solution, approximately between 1.9 and 2.3.

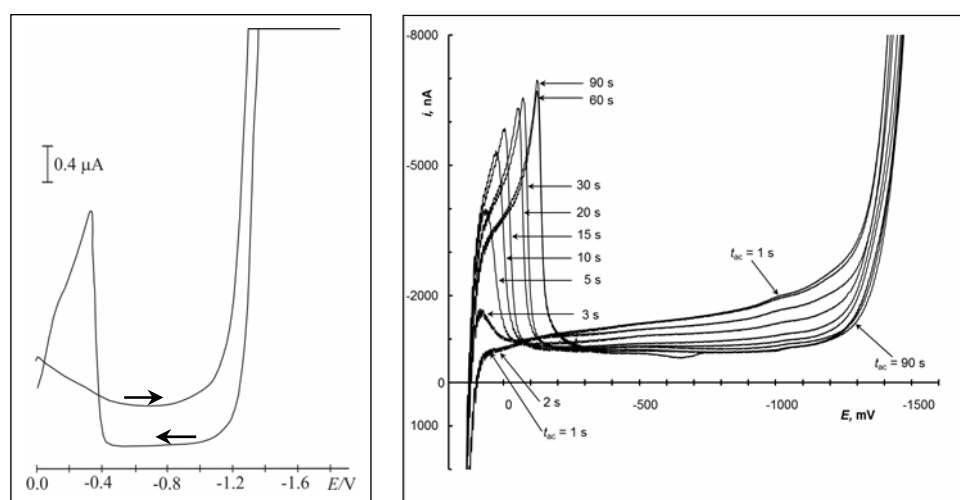


Figure 1.: Cyclic voltammogram of aqueous $1 \cdot 10^{-4}$ M HAuCl_4 solution recorded after 60 s delay at reverse potential $E_{\text{rev}} = -1.9$ V to $E_{\text{in}} = E_{\text{fin}} = 0$ V, at the rate of potential scan $v = 200$ $\text{mV} \cdot \text{s}^{-1}$

Figure 2.: Linear voltammograms of aqueous $2 \cdot 10^{-4}$ M HAuCl_4 solution recorded from $E_{\text{in}} = -1.7$ V to $E_{\text{fin}} = 0.15$ V at rate of potential scan $v = 200$ $\text{mV} \cdot \text{s}^{-1}$ and with accumulation times at initial potential $t_{\text{ac}} = 1, 2, 3, 5, 10, 15, 20, 30, 60, 90$ s.

On mercury electrode in dilute aqueous chloroauric acid at negative potentials occur two electrode reactions: at less negative potentials are reduced protons from the chloroauric acid with evolution of hydrogen, and at more negative potentials occurs complete reduction of gold from the chloroauric anion to gold atoms. Consequence of the first reaction is alkalization of the electrode/solution interface which leads to gradual changes of chloroauric anion AuCl_4^- into hydroxocomplexes $[\text{AuCl}_3\text{OH}]^-$, $[\text{AuCl}_2(\text{OH})_2]^-$, $[\text{AuCl}(\text{OH})_3]^-$ and finally into insoluble $\text{Au}(\text{OH})_3$, which aggregates into colloidal 80 - 200 nm particles [1] and adsorbs at the electrode. This adsorption causes decrease of the slope of the charging current part of the curve. The reduction of gold from the hydroxocomplexes then occurs through the layer of $\text{Au}(\text{OH})_3$ precipitate and produces gold atoms at the outer side of the layer adsorbed on mercury surface. There, according to their amount, the gold atoms partly undergo a spontaneous association into nanoparticles, partly individual atoms which penetrate through the layer of $\text{Au}(\text{OH})_3$, dissolve in mercury forming some of more than three different gold-mercury intermetallics in the amalgam [2]. The association of gold atoms in the electrode/solution interface hence proceeds through the transition stage of gold nanoparticles. Elementary gold electrodeposited in the stream of hydrogen evolution has the tendency to adsorb and absorb hydrogen [3]. If some nanoparticles formed at negative potentials can survive the surface reactions before getting amalgamated, they would react as catalysts of hydrogen evolution.

When the electrode potential moves from negative to positive potentials, the gold deposition and the hydrogen evolution stop and the electrode is exposed to the acidic solution, which gradually dissolves the adsorbed $\text{Au}(\text{OH})_3$ layer. On the clean mercury surface the amalgamation of gold particles proceeds then unhindered. The electrode reaction occurring when the potential scan nears its positive end depends on the relative rates of the involved processes - if sufficient amount of gold, produced at negative potential, is brought fast enough to positive potentials, some of the gold nanoparticles, which survive at the electrode surface before they get amalgamated, catalyze hydrogen evolution at the unusually low negative potential when the mercury surface becomes free. Hydrogen evolution on normally prepared gold amalgam electrodes takes place with overvoltage [4], however, freshly prepared gold nanoparticles are very active catalysts in heterogeneous systems, also in electrochemistry [5-7], and in hydrogen evolution [8], and hence we attribute the described positive cathodic current maximum to catalytic evolution of hydrogen by them.

Acknowledgements

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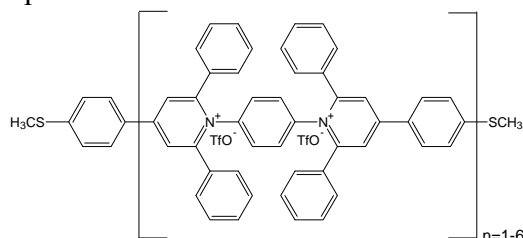
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ELECTRON DOPABLE MOLECULAR WIRES BASED ON THE EXTENDED VIOLOGENS

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Electrochemical and adsorption properties of the extended viologen molecules **1** to **6** (shown in the inset) have been studied. With increasing number of the repeating units the redox potential of the first electron transfer step shifts towards more positive potentials, reaching a constant value of -1.0V and the overall number of transferred electrons increases. The shortest molecule **1** accepts up to four electrons in four one-electron reversible redox steps due to the reduction of two identical and communicating pyridinium rings. The other



compounds in these series transfer 2, 4, 6, 8 and 10 electrons initially in two closely spaced waves. Such behaviour is consistent with a preferential reduction of the p-phenylene-4,4'-bipyridinium moieties, which are each reduced by two electrons. Number of initially transferred electrons corresponds to the number of these

units in the molecule and points to the initially non-communicating redox centres. This behaviour is in accord with the observed UV-Vis absorption bands and with the calculated Lowest Unoccupied Molecular Orbitals. LUMO of molecule **1** covers the entire backbone excluding the four phenyl substituents and the SCH₃ endgroups, whereas it is localized on the p-phenylene-4,4'-bipyridinium moiety of the molecule **2**. After chemical deprotection of the *tert*-butyl thiol derivatives, the single molecule conductivities of this homologous series have been measured by Tao's method in the gold-molecule-gold junction arrangement. The resulting conductivities of individual molecules range from 5 to 3 nS (**1** and **6**), whereas these values decrease exponentially with the wire length. The adsorption properties were studied initially on the mercury electrode surface and point to the compact monolayer formation with molecules lying flat on the electrode surface. At the electrode potential of the first electron transfer the upright reorientation process was discerned. Monolayer formation was also confirmed on the gold substrate. Feasibility of the protection of these molecules by the host-guest type of interaction was studied using cyclodextrin molecules. UV-Vis and fluorescence spectroscopy measurements confirmed the formation of two types of complexes between α -cyclodextrin and **1** with the complex formation constants $K_a = (25 \pm 3) \times 10^3 \text{ M}^{-1}$ for $[\alpha\text{CD}-\mathbf{1}]$ complex and $K_a = (2.1 \pm 0.7) \times 10^5 \text{ M}^{-2}$ for $[(\alpha\text{CD})_2-\mathbf{1}]$ complex, respectively.

Acknowledgement

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NANOBUBBLES AT SOLID-LIQUID INTERFACE

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Ambient gas nanobubbles of size ~101 - 102 nm adhering to solid phase at hydrophilic liquid/hydrophobic solid interface may contribute to rearrangement of solid surface. Spontaneous restructuring observed on multilayer graphene planes (highly ordered pyrolytic graphite, HOPG) immersed in aqueous media was investigated both in situ and ex situ by AFM and Raman spectroscopy respectively. The proposed explanation addressing room temperature non-oxidative exfoliation of graphene planes and subsequent rolling to graphene-based nanoparticles self-arranged into nano-assembly network (Fig. 1) is supported as follows: Nanostructures composing the network were resolved by HRTEM/SAED as graphene nanoscrolls, nanohorn-like and onion-like nanoparticles (Fig. 2). Nanobubbles spread over immersed HOPG basal plane (only basal plane was in contact with liquid) as imaged by in-situ AFM (Fig. 3); consequently, the morphology of nanoparticle network shows remarkable consistency with the surface distribution of nanobubbles. The AFM in situ imaging of immersed basal plane revealed formation of nanoindentations and rims at nanobubble positions and indicated ongoing surface rearrangement. The basal plane nanostructuring accorded with the intensifying D-mode in Raman spectra. No surface contamination except of ambient oxygen and nitrogen was found by XPS analysis. While the mechanism of the phenomenon is not fully clarified yet, nanobubble participation in the exfoliation by means of forces acting at the nanobubble perimeter-ternary interface can be considered. In such case however, the magnitude of nanobubble interfacial forces could exceed the value elucidated from so-called nanobubble-assisted surface “cleaning” (ETStress ~ 20 MPa) manifested as nanobubble-assisted removal and deformation of deposited thin film and adsorbed layers respectively. Accordingly, nanobubble engagement is expected in formation of nano-protrusions and nanobubble-shaped imprints on PTFE (Teflon, EYM ~ 0.5 GPa)/aqueous interface. The influence of experimental conditions including liquid phase composition on the investigated phenomenon is discussed.

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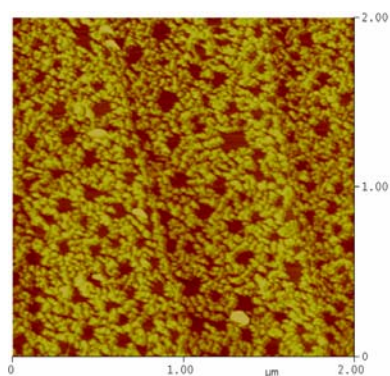


Figure 1: AFM image of graphene-based nanoparticle network formed on basal plane HOPG, $Z = 5$ nm

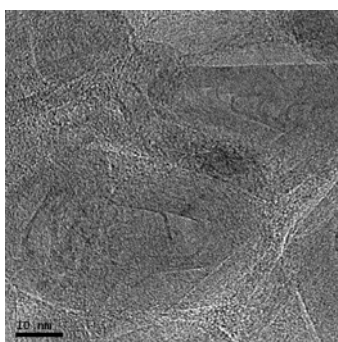


Figure 2: HRTEM image of graphene nanoparticles (from Fig. 1)

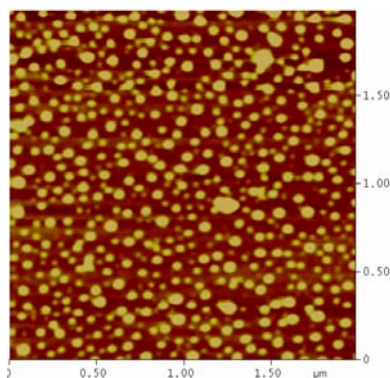


Figure 3: In situ AFM image (tapping) of gas nanobubbles covering immersed basal plane HOPG, $Z = 5$ nm

SPECTROELECTROCHEMISTRY OF GRAPHENE AND GRAPHENE LAYERS

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The latest advances in chemical vapor deposition (CVD) synthesis have now allowed the preparation of large and uniform monolayer graphene monolayers. The CVD prepared graphene thus significantly simplifies the materials processing and more detailed studies with such samples can be readily performed. The successful application of graphene requires a detailed understanding of its electronic properties, both in its neutral and doped states. The doping of graphene leads to a shift of the Fermi level and for this reason doping provides a simple way to control the transport and optical properties. In our study the electrochemical charging has been applied to study the influence of doping on the intensity of the various Raman features of chemical vapor deposition –grown graphene. Three different laser excitation energies have been used to probe the influence of the excitation energy on the behavior of both the G and G' modes regarding their dependence on doping. The intensities of both the G and G' modes exhibit a significant but different dependence on doping. While the intensity of the G' band monotonically decreases with increasing magnitude of the electrode potential (positive or negative), for the G band a more complex behavior has been found. The striking feature is an increase of the Raman intensity of the G mode at a high value of the positive electrode potential, due to partial canceling of interfering transitions, which is an important breakthrough in the understanding of the Raman process in graphene.

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SELF-ORGANIZED STRUCTURES OF METHYLATED- β -CYCLODEXTRIN ON MERCURY AND Au(111) ELECTRODE

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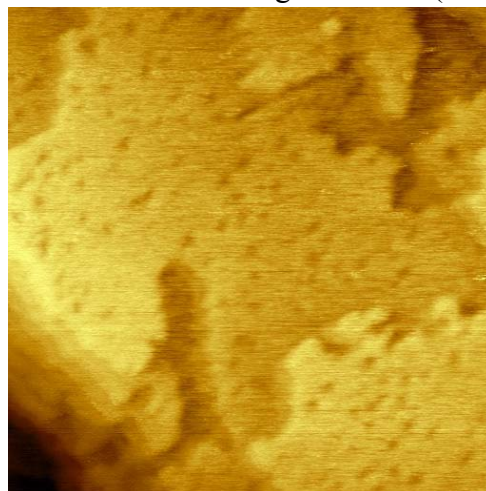
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Self-organized structures of heptakis-(2,3,6-tri-O-methyl)- β -cyclodextrin derivatized with the acetylcystein moiety (abbreviated as Me₃ β CD-NHCOCH(NHAc)CH₂SH) were investigated at the mercury|0.1 M KCl interface by the aid of ac polarography, cyclic voltammetry and ac voltammetry. For the electrode potential values less negative than -1.50 V vs. 1 M LiCl|AgCl|Ag reference electrode, the molecules of Me₃ β CD-NHCOCH(NHAc)CH₂SH were found to form an adsorbed layer. The differential capacity of the electrode interface was found not to depend on the concentration of the molecules in the bulk of the solution, suggesting the formation of a two-dimensional film.

The adsorption of Me₃ β CD-NHCOCH(NHAc)CH₂SH was further investigated on Au(111) surface by ex-situ atomic force microscopy (AFM) and scanning tunnelling microscopy (STM). The techniques showed that the molecules form aggregates with the height and width 4.2 ± 0.7 nm for the adsorption taking place under the electrochemical control. On the other hand, the adsorption based on an ultrasonic treatment leads to a well-organized monolayer (see figure), the thickness of which (1.1 ± 0.2 nm) is in a very good agreement with the characteristic dimension of the Me₃ β CD-NHCOCH(NHAc)CH₂SH molecule (1.3 nm).



Acknowledgements

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**SURFACE SEGREGATION OF THE Au₄Pd NANOPARTICULATE ALLOYS
IN ELECTROCATALYTIC REACTIONS**VALERY PETRYKIN^a, TIMO JACOB^b AND PETR KRTEL^{a,*}^a*J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 18223 Prague, Czech Republic*^b*Institute for Electrochemistry, Ulm University Albert-Einstein-Allee 47, D-89069 Ulm, Germany*

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Metals and metal alloys represent catalysts of key importance in various catalytic and electrocatalytic processes such as hydrogen evolution [1], oxygen reduction [2], or oxidation of small organic molecules (*e.g.* alcohols, etc.). The traditional approach in electrocatalysis on alloys builds on the assumption that the local structure of the catalyst (*i.e.* coordination numbers and chemical nature of bonding partners in the 1st and 2nd coordination shells) does not change during the electrocatalytic reaction. It inherently anticipates that the structural arrangements of the characteristic reaction centers are stable and present on the catalyst's surface at all times. This concept of rigid systems has been challenged by both theoretical [3] as well as experimental studies [4] describing selective adsorption-triggered segregations of the alloy components to the surface.

The present paper will focus on the application of *in-situ* X-ray absorption spectroscopy (XAS) in the EXAFS-mode to monitor the effects of hydrogen adsorption/evolution-triggered surface segregation on the local environment of the components of a model bimetal catalyst based on Au and Pd. The local structure based on the EXAFS function refinement experimentally proves the expected Pd segregation to the surface predicted theoretically. The Pd shows a tendency to form clusters at the surface upon adsorption of hydrogen. The adsorbed hydrogen also causes significant disorder, which manifests by anisotropy of the metal–metal bonds with respect to the relaxed *fcc* structure of Pd and Au. The actual bonding distances as well as Pd and Au coordination numbers will be compared with structures predicted by density functional theorem (DFT) calculations.

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ADVANCED FUNCTIONAL MATERIALS FOR ELECTROCHEMICAL SCIENCE AND TECHNOLOGY: NETWORK FILMS OF CARBON AND NOBLE METAL NANOSTRUCTURES MODIFIED WITH INORGANIC MOLECULES

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Of particular interest to the preparation of advanced materials is synthesis and characterization of carbon nanostructures (e.g. nanotubes) and noble metal nanoparticles, their stabilization (e.g. through self-assembly), as well as organization into two-dimensional arrays and controlled fabrication (e.g. through the sequential attraction) into three-dimensional network films. They can form nanosized materials with well-defined composition, structure and thickness. The interfaces can be also highly functionalized, and they can exhibit specific catalytic or unique electronic, charge storage, optical and sensing properties. We explore here the ability of inorganic structures to stabilize and derivatize metal and carbon nanostructures. Among inorganic systems, polyoxometallates of molybdenum and tungsten are attractive since they can not only adsorb irreversibly on solid surfaces but also exhibit reversible stepwise multielectron transfer reactions. The concept of the layer-by-layer formation of hybrid (organic-inorganic) assemblies composed of anionic polyoxometallate-protected carbon nanotubes (or metal nanoparticles) and ultra-thin films of positively charged conducting polymers (e.g. such as polyaniline or PEDOT) will be described and discussed here. The resulting novel composite materials have been fabricated as thin or moderately thick (μm level) films on electrode surfaces. As evidenced from STM and scanning electron microscopy, their morphology is still granular but the structure is fairly dense. Further, they are characterized by fast dynamics of charge propagation. Obviously, this research is of importance to the construction of effectively operating charge storage devices (capacitors), charge mediators (e.g. in bioelectrochemistry), molecular electronic systems and electrocatalysis. In the latter case, polyoxometallates can also be applied to stabilize and link Pt-Ru, Pt-Sn and various alloyed Pt-based nanoparticles. It is apparent from diagnostic cyclic voltammetric, rotating disk voltammetric and chronoamperometric measurements that such systems exhibit attractive properties towards electroreduction of oxygen or oxidation of alcohols (ethanol, methanol). Here, it is possible that addition of polytungstate or molybdate clusters to ruthenium or tin hydroxo species at the catalytic interface results in activating effect on dispersed platinum particles. An alternate explanation may involve a possibility of electronic effects and/or different morphologies of the catalytic films in the presence and absence of polyoxometallate.

**DEPENDENCE OF FLICKER NOISE
ON THE SURFACE STRUCTURE OF MICROELECTRODES**

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The noise theories developed for electronic devices have been adapted to electrochemistry for nearly four decades. However, partially due to the low noise levels of usual redox electrodes, partially due to the lack of high power personal computers and cheap, high performance data acquisition systems, the noise investigations on fundamental electrochemical systems practically have not carried out even until now – the interest of researchers concerning electrochemical noise turned to corrosion phenomena which yield a considerably higher noise level.

In our previous works we made an attempt to study the shot noise of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction, and as a second step, the noise of hydrogen evaluation reaction on microelectrodes. Based on the strong correlation between noise and impedance, we concluded that noise measurements should always be combined with impedance measurements. We also proposed a new measure for noise, namely the relative noise power density spectrum (S_{rel}). It is expressed as the ratio of the measured voltage or current noise spectrum and the thermal noise spectrum formally calculated from the real part of the measured impedance (admittance) of the system:

$$S_{rel}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} \equiv \frac{S_I(\omega)}{4kTY'(\omega)}$$

According to the usual definition, a random process is considered to provide flicker noise if the noise spectrum ($S_U(\omega)$ or $S_I(\omega)$) is proportional to $1/\omega^\alpha$. In contrast to this view, we define flicker noise as a $1/\omega^\alpha$ behaviour only of the relative noise spectrum ($S_{rel}(\omega)$), i.e. when we observe such a phenomena that is not present in the corresponding impedance data.

The origin of flicker noise is usually attributed to either inhomogeneity of the electrode surface, or to the random fluctuation of the concentrations of the free charge carriers. In the present work the effect of different surface preparations of microelectrodes was studied on the obtained flicker noise of redox electrode reactions.

EXPLORING PATHS TOWARD MORE EFFICIENT SOLAR CELLSJOSEF MICHL^{a,b,*}^a*Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, U.S.A.*^b*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague, Czech Republic*

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The development of solar cells that are both inexpensive and efficient is an essential ingredient of efforts to prevent the worst consequences of continued combustion of fossil fuels. There are two ways toward the goal, either using a single junction cell operating closer to the Shockley-Queisser limit of $\sim 1/3$ maximum theoretical efficiency, or finding a simple way of avoiding this limit. Singlet fission, a process in which one absorbed photon permits the generation of two excited triplet states and thus ultimately of two electron-hole pairs, is one of the possibilities for the latter approach. Combined with the use of an ordinary sensitizer, the application of a singlet fission sensitizer would move the theoretical efficiency limit close to $1/2$. At the moment, only very few materials have been shown to perform singlet fission efficiently, and if practical sensitizers are to be developed, it would be very useful to have design guidelines for their synthesis. We work on the fundamental understanding of the phenomenon and are attempting to use first principles to develop design guidelines in three steps; identifying: (i) optimal chromophores, (ii) optimal modes of chromophore coupling, and (iii) optimal structures that favor charge separation. The description of the design guidelines will be followed by examples of their testing, which has so far led to a $\sim 50\%$ triplet yield in a thin film in one and a 200% triplet yield in another new crystalline material.

**THIOL NANOLAYERS AT MERCURY AND AMALGAM ELECTRODES.
CHRONOPOTENTIOMETRIC DETECTION OF CHANGES
IN PROTEIN STRUCTURES AT PICOMOLE LEVEL**

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Important features of nanoscale bioelectrochemistry involve two-dimensional organization of biomolecules on electrodes. Monolayers of DNA and proteins can be formed by thiolate-containing DNA or proteins either at bare electrodes or by immobilizing proteins on self-assembled monolayers (SAMs) of thiolates. Recently we have proposed dithiothreitol (DTT)-mercury and DTT-solid amalgam electrodes for protein microanalysis by means of constant current chronopotentiometric stripping (CPS). At the DTT-modified hanging mercury drop electrode (DTT-HMDE) [1] proteins at nanomolar concentrations produce the CPS peak H, which is due to the protein catalyzed hydrogen evolution [2-12]. Self-assembled monolayers (SAMs) of DTT at the electrode surface protect surface-attached proteins from the electric field-driven denaturation, but do not prevent the electrocatalysis. Using CPS peak H native and denatured forms of bovine serum albumin (BSA) and of other proteins were easily distinguished. On the other hand, in usual slow scan voltammetry (scan rates between 50 mV and 1 V/s) the adsorbed BSA behaved as fully or partially denatured. BSA-modified DTT-HMDE was exposed to different potentials, E_B for 60 s, followed by CPS measurement. Three E_B regions were observed, in which either BSA remained native (A, -0.1 to -0.3 V), was denatured (B, -0.35 V to -1.4 V) or underwent desorption (C, at potentials more negative than -1.4 V). At potentials more positive than the reduction potential of the DTT Hg-S bond (\sim -0.65 V against Ag|AgCl|3M KCl) the densely packed DTT SAM was impermeable to $[\text{Ru}(\text{NH}_3)_6]^{3+}$. At more negative potentials the DTT SAM was disturbed but under conditions of CPS (with very fast potential changes) this SAM still protected the protein from surface-induced denaturation. Thiol-modified Hg electrodes in combination with CPS represent a new tool for protein analysis.

We applied this method for studies of the effect of oncogenic mutations on the DNA-binding domain of the tumor suppressor p53 [13]. The CPS responses of wild type and mutant p53 showed excellent correlation with structural and stability data and provided additional insights into the differential dynamic behavior of the proteins [14, 15]. Further, we were able to monitor the loss of an essential zinc ion resulting from mutation (R175H) or metal chelation. We envisage that our CPS method can be applied to the analysis of virtually any protein as a sensor for conformational transitions or ligand binding to complement conventional techniques, but with the added benefit that only relatively small amounts of protein are needed and instant results are obtained. This work may lay the foundation for the wide application of electrochemistry in protein science, including proteomics and biomedicine.

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LOCAL STRUCTURE AND ITS EFFECT ON ELECTROCATALYTIC BEHAVIOUR OF NANOCRYSTALLINE RuO₂ BASED MATERIALS

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Recent theoretical works [1,2] on electrocatalytic O₂ and Cl₂ evolution on rutile-type oxides link the activity and selectivity in those processes to the cation stacking along the direction of c-axis. This order can be effectively altered by substitution of Ru in RuO₂ host by 3d metals such as Fe, Co, Ni or Zn. In particular, Ru_{1-x}Ni_xO₂ and Ru_{1-x}Zn_xO₂ materials exhibit opposite trends in terms of selectivity of chlorine and oxygen production, presenting interesting examples of local and electronic structures effects on catalytic performance of the materials. At the same time, the nature of “active sites” in both materials for both gas evolution processes is poorly understood due to the lack of structural information for these doped RuO₂ based oxides.

In this work local structure of Ru_{1-x}M_xO₂ (M=Ni and Zn; x=0.0-0.3) materials was examined by X-ray absorption spectroscopy (XAS) using the data collected on Ru-K, Ni-K and Zn-K edges. Visual comparison of the EXAFS functions revealed that the local structure around Ru core atoms undergoes only little change with increase of a dopant concentration. At the same time, the variation of Ni and Zn content results in rather dramatic evolution of Ni- and Zn-EXAFS functions and appearance of new features in the spectra that cannot be interpreted in terms of atomic arrangement in conventional rutile structure.

Full-profile refinement of EXAFS spectra revealed that for low Ni concentration the materials structure can be described in terms of Ni substitution into Ru site of RuO₂, which conforms to rutile structure. Ni tends to occupy metals sites along the diagonal of rutile unit cell, and the deviation of site occupancy from the statistically expected values indicates possible tendency of Ni towards clustering. For Ru_{1-x}Ni_xO₂ materials with x>0.1 Ni concentration, local structure around Ni cannot be explained in terms of substitution only, and one should assume formation of defects with rock salt motif in the vicinity of Ni. Such defects formation may be explained in terms of shear planes, which are common for the oxygen deficient rutile. The materials with Zn doping were found to be metastable with respect to the decomposition and at high zinc concentration they tend to realize another type of Zn-rich defect regions, which conform to the ilmenite structure within RuO₂ host. The revealed differences in the architecture around doped cations along with in situ XANES and the differences in the selectivity among two types of materials helped to understand the processes of the electrochemical evolution of chlorine and oxygen on these materials.

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**MOLECULAR AND SPIN DYNAMICS IN PRISTINE
AND CHARGED ENDOHEDRAL METALLOFULLERENES**

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Depending on the carbon cage as well as the type of the encapsulated species (single metal atoms, two or more metal atoms, clusters of metal atoms with non-metals like nitrogen, oxygen, sulfur, etc) endohedral metallofullerenes (EMFs) exhibit different types of bonding with dynamic regimes varying from the tight fixed position of the endohedral species inside the carbon cage to a nearly free rotation. Dynamics of the internal species can be also significantly altered by charging the EMF molecule and its chemical modification by the exohedrally attached functional groups. In the case of radicals, dynamics of the spin density is also strongly affected by the motions of the endohedral cluster.

The cluster dynamics seriously affects spectroscopic properties of the EMFs and their derivatives such as, for instance, ESR spectra of the radicals. In case of rotation of the cluster, experimentally measurable properties correspond to the time-averaged situation (the time scale can reach nanosecond diapason as in ESR and NMR spectroscopies) and prediction of such properties by static DFT computations can be even qualitatively incorrect. Thus, when predicting the spectroscopic properties, this kind of internal dynamics should be taken into account. In most cases nowadays, the information on the dynamics of endohedral clusters is revealed either through the ordering of single-crystal X-ray structures (the EMFs with "free rotation" of the cluster exhibit disordered structures) or through DFT computations of the possible cluster configurations, which show many almost isoenergetic minima for EMF molecules with free rotation and noticeable difference of the energies of such conformers in the case of hindered rotation. These methods provide only qualitative conclusions and do not give detailed information on the cluster behavior.

Molecular dynamics (MD) simulations, which allow direct "observation" of the dynamic behavior of the species on the microscopic scale, appear to be an ideal tool for addressing the problems of the cluster dynamics and its influence on spectroscopic properties. However, the wide use of such methods is still hindered by the high computational costs, especially when long propagation times are necessary. For this reason, first principle MD studies of endohedral fullerenes are still very rare. In this work we report on the detailed MD study of the set of EMFs in their neutral and charged forms and discuss how dynamics of the cluster affects dynamics of the spin density distribution and ESR spectra. We show that even small displacements of the cluster can result in dramatic changes in the spin density distribution, the effect we dubbed as "spin-flow". Fourier-transformation of spin-populations gives then "spin-flow vibrational spectra", which showing how spin flow is coupled to specific vibrations of the molecules.

EXTENDED VILOGENS: MOLECULAR WIRES AS A SOURCE OF OSCILLATIONS

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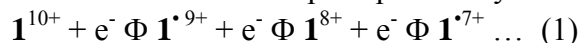
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Oscillations of the electric current or potential have a fundamental importance in the electronic technology and digital systems. Counting, timing and synchronization of all kinds of repetitive events is provided by oscillators. Rapidly developing field of molecular electronics sooner or later has to deal with a possible design of molecular oscillators. Oscillations of the tunneling current were observed during the STM imaging and molecular conductivity measurements of the viologen-type compounds. It was speculated that their origin is connected with the heating and cooling of the tunneling gap. Nevertheless, a sound explanation is still lacking. Sources of the periodic events are found also in chemistry and operate in very diverse systems. The most common chemical systems investigated for reaction mechanism are those which monotonously proceed from initial reagents to final products. Few rather curious examples of autocatalytic or autoinhibitory redox reactions deviate from such simple routes. Instead, numerous oscillatory effects may be observed. Chemical community pays relatively little attention to alternating reactions regardless of its wide-spread mode of action in periodical processes in the natural systems. A biochemical circadian oscillator in living organisms may serve as one of the many very complex examples [1]. The electrochemical oscillations caused a periodic evolution of hydrogen bubbles during the dissolution of iron in acids, which was probably the first report on a periodic behavior [2] made as early as in 1828. Later numerous examples of passivation-activation cycles from the field of the corrosion science were described [3]. Spontaneous oscillations occur also in the heterogeneous catalytic [4] and electrocatalytic reactions [5-7]. A common feature of all electrochemical oscillators is the existence of the negative differential resistance [8] in the electrochemical impedance spectrum. Notion that many systems can change its state from stability to periodicity and to chaos was for a long time puzzling until in the 1970's rigorous mathematical theories were developed [9] and later applied in chemistry and physics.

This communication describes electron transfers in octo- and deca-cation of the “extended viologen” **1**, which contain four or five reducible repetitive bipyridinium functions (Fig.1). We expected that compound **1** will show a communication of redox centers. Surprisingly the faradaic current in the vicinity of the first formal redox potential(s) is very irregular [10, 11]. In an attempt to clarify the origin of the irregular currents we found that this redox system yields oscillations without any additional external impedance. The frequency and the form of oscillations are very sensitive to the applied potential (Fig.2). Furthermore, under the strict values of parameters it produces a sine-wave current (Fig.3). This property makes **1** a good candidate for application as a ‘molecular oscillator’. The oscillating system described here involves just a single compound. It is much simpler than other electrochemical oscillators, which usually include a redox active component and either a catalyst or an inhibitor. However, the simplicity of **1** is only apparent. In a formal way we can consider that ten

reducible pyridinium functions in the decacation **1** offer many different ways, how those five bipyridinium units accept the electrons. The simplest possibility is a stepwise mechanism



If we denote a pyridinium unit in its oxidized state by zero (0) and in the reduced state by one (1) then the redox state of a bipyridinium unit can be represented by two digits as 00, 10, 01, and 11. For example the products of a three-electron reduction to $\mathbf{1}^{\cdot 7+}$ in the above equation can contain several combinations of redox forms of its five bipyridinium functions 00-10-10-10-00, 10-00-10-00-10, 10-00-01-00-01, etc.

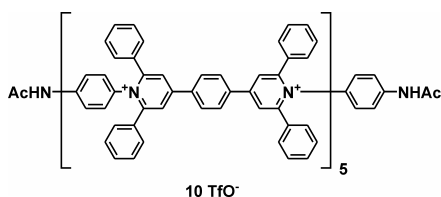


Figure 1: Structure of extended viologen

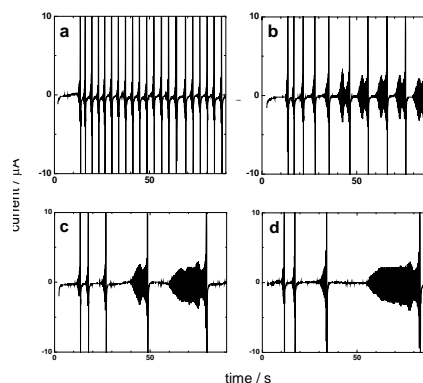
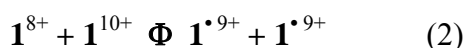


Figure 2: Current-time series at different applied potentials

The full step-wise two-electron reduction of all bipyridinium units would formally amount to 511 ($=2^{(10-1)}$) combinations of the different intermediate redox states of **1**. A further complexity stems from the disproportionation and comproportionation reactions between various partially reduced forms and the parent compound diffusing to the electrode. These surface homogeneous redox exchange reactions in the reduction of bipyridinium-type compounds have been confirmed. One of the cross redox reactions in the present system certainly is



We interpret the observed periodic faradaic currents as a result of the coupling of the heterogeneous and homogeneous charge transfer processes. Indeed, this is supported by our preliminary simulation using a model based on Eq. 1 and 2.

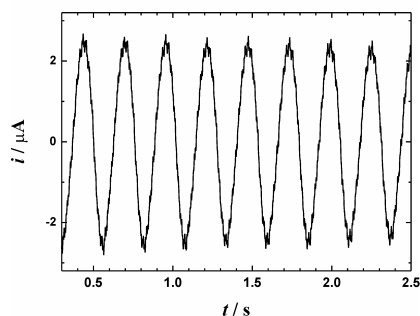


Figure 3: Sine-wave oscillations at a constant potential -0.590 V.

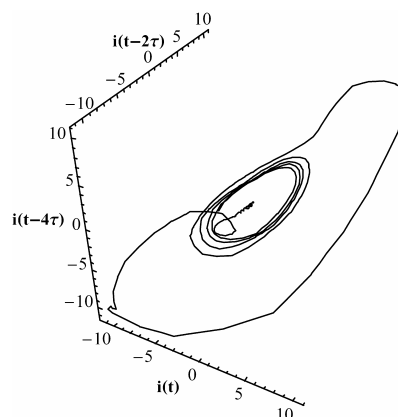


Figure 4: Reconstructed attractor from the current-time series at -0.575 V.

Rather complicated time series in Figure 1 show the transfer of the system from periodicity to a deterministic chaos. A deterministic process yields time series, in which a value observed at time t is determined by a preceding value even though the functional dependence may not be known. This contrasts the random events producing time series with mutually uncorrelated adjacent values. The three dimensional time delay portrait in Figure 4 shows a spiraling transition to an attractor orbit and proves that irregular current fluctuations have the attributes of the deterministic chaos. The character of a deterministic chaos was confirmed by evaluation of the Ljapunov exponent [12] λ , which quantifies an exponential divergence of orbits. We obtained the positive value of the exponent $\lambda=0.41 \pm 0.05$ indicating thus the presence of the deterministic chaos. The system dynamics therefore has a functional dependence though it is still unknown. On the contrary, the random current fluctuations would fill the space of a time delay diagram without any structure.

The dynamics of the system can be controlled and forced to sinusoidal oscillations or to stability. This type of a molecular structure could be explored as a component of a molecular oscillator. Periodic and chaotic effects observed during the electron transfer process do not disqualify oligomer **1** and similar extended viologens from its originally expected application as a molecular conductor.

Acknowledgement.

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**THREE DIMENSIONAL CONSTRUCTION OF ELECTRODES -
OPEN DOOR TO HIGH CAPACITY LITHIUM BATTERIES**

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The thin-film lithium battery technology has made a significant progress in the past ten years and in many aspects it has reached the theoretical possibilities. While the thin-film battery is nearly optimized, the capacity limits of lithium accumulators can be further extended by an original construction of 3-D electrodes. The 3-D design with electrodes several millimeters thick allows new features that have not been used in the battery industry yet. 3-D concept of the accumulator not only increases the capacity of individual cells but also significantly reduces the size of the assembled modules. Construction of prototypes and their electrochemical performance will be demonstrated.

PERFORMANCE OF BUCKY-GEL ACTUATORS BASED ON SINGLE-WALLED CARBON NANOTUBES AND IONIC LIQUIDS

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For the development of artificial muscles, polymers present an interesting alternative to conventional technologies. They possess inherent compliance, are light, and are generally cheap. In order to improve the performance, the use of carbon nanotubes (CNTs) as active materials for electrochemical actuators is of interest. CNTs have attracted much interest because of their intrinsic mechanical and electrical properties, and the possibility of functionalizing them and incorporating them in composite materials. When a bias voltage is applied between the CNTs and a counter-electrode, the CNTs can elongate due to double-layer charge injection. Also, ions migrate to the surface of the CNTs. The resulting charge build-up must be offset by a rearrangement of the electronic charge within the tubes. The actuation is then due to Coulombic forces between inserted ions and CNT walls.

In this communication, we report high-performance bucky-gel electrochemical actuators incorporating various amounts of single-walled carbon nanotubes (SWCNTs) and ionic liquid electrolytes, mainly imidazolium based ionic liquids. These actuators show stable electromechanical responses and behave as flexible supercapacitors [1]. The displacement caused by an applied sinusoidal voltage and electrochemical impedance spectroscopy are used to analyze the electromechanical behavior of bucky-gel single-walled carbon nanotube actuators containing an ionic liquid.

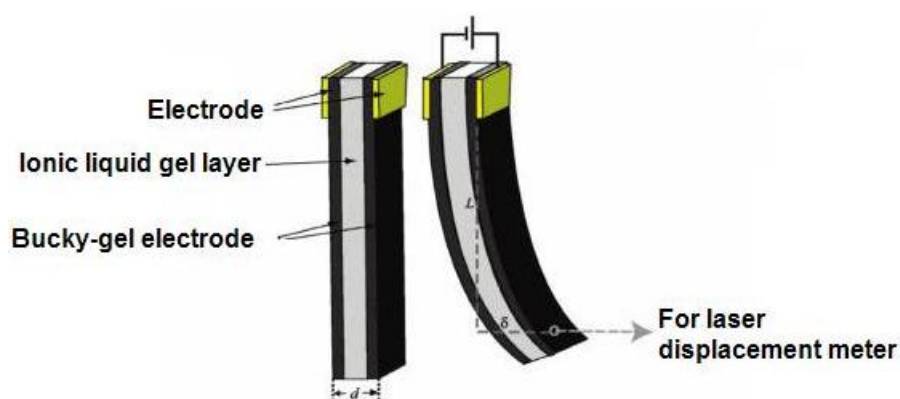


Figure 1: Schematic drawing of bucky-gel actuator.

The electrochemical behavior can be understood in terms of complex capacitance diagrams and the frequency dependence of the real and imaginary components of the capacitance [2]. The complex power allows analyzing the relationship between energy storage and energy dissipation during the operation of the electrochemical actuator. Furthermore, the energy-power plot or Ragone plot that expresses the useable energy as a function of the power is determined. The relationships between the electrochemical and mechanical properties of the

devices strain-energy-power plots are analyzed by means of strain-energy-power plots. The maximum power P_{\max} and specific energy densities E_{\max} of the electrochemical actuator are calculated. The energy densities of bucky-gel SWCNT actuators containing an ionic liquid are higher than those of natural muscles. In order to achieve high energy and power densities, the approach proposed here will help to a better understanding the actuation processes and for optimizing the device performance.

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**REASSESSMENT OF THE KRAMERS-KRONIG RELATIONS
IN THE CONTEXT OF THE STABILITY OF THE TITANIUM ELECTRODE**

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The activation and anodization of Ti electrode is effectively monitored by recording its electrochemical impedance (EI). Good EI spectra recorded on stable electrode allow determination of oxide layer capacitance. From this its dielectric constant can be evaluated, if its thickness is known from independent measurement. Similarly, its thickness can be evaluated, provided the dielectric constant is known. In most cases recording the EI spectra causes no problems. However, when there structuring of the oxide layer occurs, emerge instabilities. Then validity of EI spectra has to be verified carefully by Kramers-Kronig relations. We have shown how to verify KK transformation for galvanostatic and potentiostatic polarisation.

TiO₂ NANOTUBES AND OTHER SELF-ORGANIZED ANODIC STRUCTURES: FORMATION AND APPLICATIONS

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The presentation demonstrates approaches to achieve electrochemical fabrication of self-organized high aspect ratio titanium oxide layers with robust meso-scale feature sizes.

Several highly promising geometries, nanotubular, nanochannel and nanosponge materials, are being compared. These different self-organized morphologies can be produced by anodic oxidation of Ti metal surface. The resulting different oxide morphologies have considerably different physical chemical and mechanical properties.

Titanium oxide is a highly functional material and has, for example, unique semiconductive and surface catalytic properties and provides a high degree of biocompatibility. Therefore it has a high potential for various technological exploitation. The talk will address synthesis and applications of the different TiO₂ nanoscale architectures.

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GROWTH OF ADSORPTION LAYER OF BENFLURALIN ON THE SURFACE

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Benfluralin (N-butyl, N-ethyl, 2,6-dinitro, 4-(trifluoromethylaniline) is a dinitroaniline herbicide registered for use on lettuce. It acts by the microtubule assembly inhibition. Most of pesticides and their metabolites are very stable in soil. Their accumulation at the interface plays an important role in the contamination of environment. The pesticides can remain in the surface layers of soil, where they are exposed to the activity of microorganisms and photoprocesses, or instead penetrate to the ground water and contaminate sources of drinking water. Processes, which take place at the electrochemical interface, often involve adsorption. The adsorbate-surface and adsorbate-adsorbate interactions participate in the formation of 'compact' layer. The capacitance of the double layer of electrode reflects very sensitively changes of the interface structure at the surfaces. This allows discrimination of a simple adsorption process and a slow transition of structure of adsorption film controlled by the mechanism of nucleation. The aim of this contribution is to obtain the information about nucleation kinetics and mechanism of growth of the film on the electrode from the time dependence of the double layer capacitance. The phase transition may lead to the reorientation within the adsorbed layer. These measurements are performed on the mercury drop electrode.

The ability of benfluralin molecules to form an adsorbed layer was studied at single crystal gold(111) electrode. The scanning probe techniques (atomic force microscopy AFM and scanning tunneling microscopy STM) were used for characterization of the layer of benfluralin on the gold(111) substrate. The height of the layer was characterized by AFM nanoshaving technique.

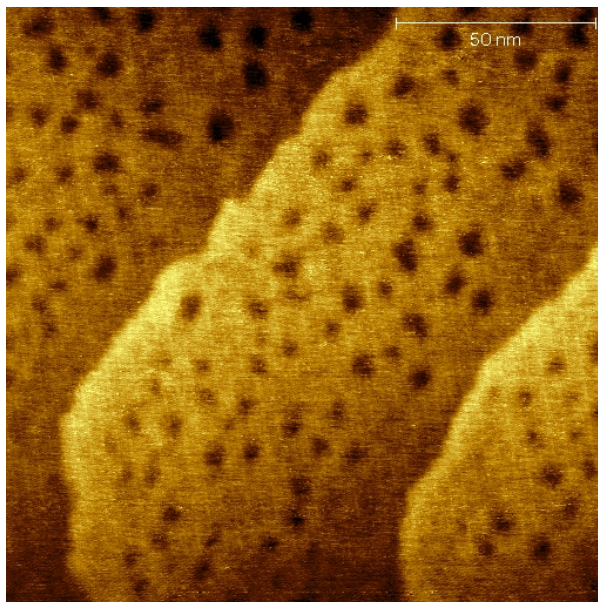


Figure: Scanning probe image of the benfluralin layer on gold(111)

Acknowledgements

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DIKETO-PYRROLO-PYRROLES FOR ORGANIC ELECTRONICSMARTIN VALA^{a,*}, MARTIN WEITER^a, STANISLAV LUŇÁK^b AND JAN VYŇUCHAL^c^a Faculty of chemistry, Brno University of Technology, Purkyňova 464/118, CZ-612 00 Brno, Czech Republic,^b Faculty of Chemical Technology, University of Pardubice, Studentská 95, CZ-530 09 Pardubice, Czech Republic^c Research Institute of Organic Syntheses, Rybitví 296, CZ-533 54 Rybitví, Czech Republic

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Introduction

Derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, commonly referred to as DPPs, constitute recent industrially important class of high-performance pigments [1], see the parent molecule in Figure 1. They are endowed with brilliant shades (ranging from yellow-orange to red-violet) and exhibit exceptional chemical, heat, light, and weather fastness. Furthermore, some of their physical properties such as high melting points are exceptional in view of the low molecular weight relative to pigment standards. It has been shown that DPP units introduced into various materials e.g. polymers, dendrimers, polymer-surfactant complexes, and oligomers results in deeply coloured, highly photoluminescent and electroluminescent materials. Due to their interesting properties, there is wide range of possible applications which have been already investigated covering for example latent pigment, charge generating materials for laser printers and information storage systems, solid-state dye lasers or gas detectors.

In order to tune the DPPs properties, we modified the basic structure by introduction of electron donating and/or withdrawing groups. Furthermore, solubilising groups (*N*-alkylation) were attached to enable solution based deposition techniques, see Figure 1. The influence on absorption and fluorescence is discussed and faced with the results obtained by quantum chemical calculations. Model electronic devices were prepared and characterized.

Results and discussion

Introduction of electron-donating groups increased the molar absorption coefficient (ϵ) and was accompanied with strong bathochromic shift. This behaviour implies that charge separation occurs via electron delocalization leading to creation of permanent dipole moment. Blurring of vibration structure in absorption spectra of mono substituted derivatives imply interaction with polar dimethylsulfoxide (DMSO) and shows polar character of the mono substituted DPPs.

Introduction of the *N*-alkylation led to the decrease of the ϵ and hypsochromic shift. First *N*-alkylation causes only small change, whereas second alkylation lead to the value of ϵ almost similar to the parent, non *N*-substituted, DPP. This decrease is accompanied by the hypsochromic shift and loss of vibrational structure. We proposed the same mechanism as for the *N*-alkylated only derivatives [2]: the *N*-alkylation causes rotation of the phenyls (see the angles α and β in Figure 1) and consequently breaks the molecule symmetry. This causes decrease of the effective conjugation and increases the polarity.

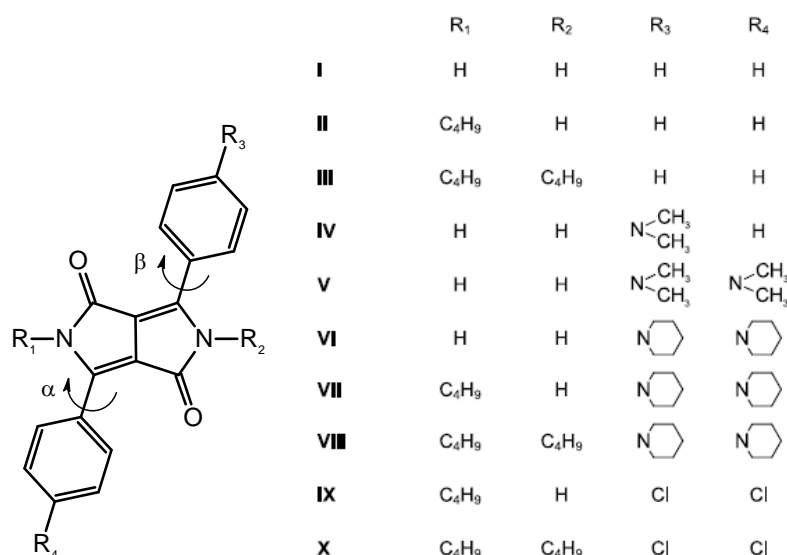


Figure 1: The basic structure of 3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4 dione, also known as DPP (structure I) and the prepared derivatives.

To test the derivatives performance in electronic devices, thin films were prepared by spin-coating (soluble derivatives) and by vacuum evaporation (not soluble derivatives). The key impact on the morphology of thin layers was found to be based on the *N*-substitution of central DPP unit by alkyl side chains. The main role plays the type of substitution: the unsymmetrical (one substituted alkyl chain) or symmetrical (two substituted alkyl chains). The symmetrically substituted derivatives form planar large crystallites with sizes increasing up to 1 μm , whereas the asymmetrically substituted derivatives form highly rough fiber crystallites.

On the basis of the findings described above symmetrically substituted derivatives resulted as suitable for electrical characterization. The prepared organic diode like devices from the phenyl di-piperidino substituted *N,N*-alkylated DPP (structure VIII) showed reasonable electroluminescence signal (the turn-on voltage for this diode was $\sim 3\text{V}$). The derivative III showed increased current flow under illumination by white light, indicating charge carrier photogeneration. Charge carrier mobilities were determined using organic field effect transistors. The obtained values were in the range 10^{-7} to $10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.

Acknowledgement

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OXIDIZED AND REDUCED ADSORPTION SITES ON AG NANOPARTICLE SURFACES

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SERS spectroscopy is currently a well established spectroanalytical method with a wide range of applications and a challenging ability to reach single molecule detection level [1]. In our research, we employ SERS spectroscopy of selected adsorbates for investigation of adsorption sites available on surfaces of chemically prepared Ag NPs (both native and chemically modified), as well as on the surfaces of Ag NPs generated by optically induced processes, such as laser ablation.

The presence of two types of adsorption sites on chloride-modified Ag NPs were initially reported in [2]. For their identification, we employed 2,2'-bipyridine (bpy) as the probe adsorbate in a series of experiments following the chloride-modification of Ag NPs as well as their generation in a strongly reducing ambient, and we evaluated the results with help of factor analysis of spectral sets [3]. We found out that (i) on the surfaces of Ag NPs weakly stabilized by adsorbed borates (native NPs prepared by borohydride reduction), only Ag⁺-bpy species spectrally identical with [Ag (bpy)₂]⁺ are present, while (ii) on chloride modified surfaces and in the strongly reducing ambient, a new surface complex Ag(0)-bpy has been identified. In contrast to Ag⁺-bpy, Ag(0)-bpy exhibits a photoinduced CT at 540 nm [4]. Further investigations revealed that once the Ag(0) sites are stabilized by bpy, the resulting Ag(0)-bpy species is quite resistant against oxidation [3]. By contrast, in the absence of a stabilizing adsorbate, Ag(0) sites are prone to oxidation [5].

Recently, we have involved SERS spectral probing into investigation of the progress of an intermittent laser ablation (LA) of a Ag target in aqueous solutions of adsorbates by nanosecond laser pulses. LA of Ag in aqueous ambient performed by nanosecond laser pulses is known to be accompanied by Ag NP fragmentation (NF), i.e. by a size-reduction of the growing NPs due to laser pulse absorption and a subsequent breaking into fragments [6]. While LA of Ag in pure water is already well known for producing Ag NPs with “chemically pure” surfaces, LA in adsorbate solutions can open a pathway to one pot syntheses of hybrid systems, such as dye-modified Ag NPs or Ag NP/polymer composites. On the other hand, such possibility could actually be hampered by a decomposition of the organic species during LA/NF.

Owing to the possibility to readily identify its surface species by SERS, bpy has been selected as a “pioneering” probe adsorbate in these studies. Ag NPs / bpy systems resulting from each of five steps of the intermittent LA/NF process with 1064 and 532 nm pulses were probed by SERS at 514.5 nm excitation (Fig.1), as well as by SPE (surface plasmon extinction) measurements.

Spectral marker bands of both Ag⁺-bpy and Ag(0)-bpy were found in the SERS spectra after the first step, while only the Ag⁺-bpy bands were present in the subsequent ones. Importantly, no other bands attributable to a decomposition product of bpy have been observed.

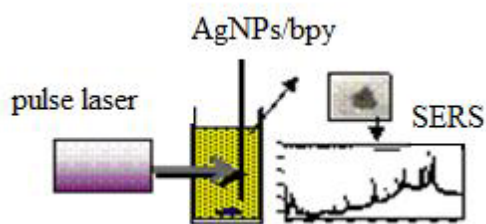


Figure 1

Concerning the Ag(0) sites formation, we propose tentatively that they originate during Ag NP growth from the primary products of LA, which are Ag atoms, Ag_n^+ species and ejected electrons, as well as larger metal clusters [7]. In the presence of bpy, these sites are readily stabilized by Ag(0)-bpy surface species formation. Concerning the disappearance of this species in the later stages of LA/NF, the most probable mechanism is a thermal decomposition of Ag(0)-bpy surface species due to the heating of Ag NPs by absorption of laser pulses prior to their fragmentation, followed by the Ag(0) to Ag^+ free-sites conversion. This conversion can proceed either by a spontaneous oxidation of the adsorbate-free Ag(0) (owing to a slow diffusion of bpy molecules to the fragmented NPs), or possibly also by a positive charging of AgNPs due to Ag^+ formation (accompanied by electron ejection) during NF [8].

Acknowledgement and Note

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CHARGE TRANSPORT WITH SINGLE MOLECULES AND CLUSTERS: AN ELECTROCHEMICAL APPROACH

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The electron transport through molecules has received great attention since organic structures have been considered as the active part in electronic nano-scale devices [1]. Different experimental set-ups allowed integrating single molecules and nanocrystals in electronic circuits. Examples are mechanically controlled break junctions (MCBJ) or scanning tunneling probes based break junctions which enabled basic investigations of correlations between molecular structures and transport properties on a single molecule level under UHV conditions at low and ambient temperatures, but also at electrified solid/liquid interfaces [2]. The latter allow applying the concept of “electrolyte gating” in a transistor-analog configuration. These studies depend, among others, on parameters such as (i) the formation of a reproducible and stable contact between the tailored molecule and both metal electrodes, (ii) the structure and the conformation of the bridging molecule and (iii) the algorithms used for the analysis of the raw data.

In this report we will focus on single molecule conductance studies in Au | molecule (cluster) | Au junctions based on a STM configuration [3] in solution as well as under electrochemical conditions. We will discuss results with α,ω -substituted biphenyls with specific focus on the role of the terminal anchoring groups and the torsion angle between the two planar phenyl rings [4]. The concept of redox-mediated gating in symmetric and asymmetric molecular junctions will be illustrated in a case study with perylene tetracarboxylic bisimide derivatives [5]. The experimental data will be compared with simulations based on the phenomenological theory of electron transfer and quantum chemical up-initio calculations [3,6]. Finally, we will compare these single redox-molecule mediated transport experiments with multi-level gating studies employing immobilized nanocrystal hybrid assemblies [7,8]. The talk will conclude with a perspective outlook.

Acknowledgement

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POSTER PRESENTATIONS

PHOTOCATALYTIC PROPERTIES OF PARTICULATE LAYERS PREPARED FROM VARIOUS TiO₂ POWDERS

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Heterogenous photocatalysis represents promising method for the decomposition of stable pollutants (dyes, herbicides, VOC etc.). For a powder photocatalyst, the photocatalytic degradation of organic pollutants proceeds faster in aqueous solution than on its immobilized layer. However particulate layers are more appropriate due to the easy preparation and no necessity of photocatalyst separation. Thus this work deals with the photocatalytic activity of several commercial TiO₂ powders deposited by sedimentation from aqueous suspension followed by calcination at 300°C. Photocatalytic activity was determined using Acid Orange 7 of initial concentration 1×10^{-4} mol/dm³ as a model compound.

The measured first order rate constants of Acid Orange 7 degradation are shown in Fig. 1. The highest activity was observed for material AV-01 which has smallest surface area (10 m²/g). Unfortunately, this layer was not sufficiently mechanically resistive i.e. particles could be removed by stream of water. Layers prepared from powders produced by Evonik-Degussa (P25, P90) and Kronos (vlp7000, vlp7001, uvlp7500) showed similar photoactivity but different resistibility. Layers prepared from P25 and P90 were mechanically more stable. That is why these materials can be considered as most appropriate for the preparation of stable particulate films with reasonably high photocatalytic activity.

Diffuse reflectance spectra of powder materials were measured to quantify their band gap energies (E_g) (as shown in Fig. 2 for powders produced by Kronos). It can be seen that vlp 7000 and 7001 absorb over 400 nm while uvlp7500 absorbs only in UV region. E_g values corresponding to anatase phase were for powders uvlp7500, vlp 7000 and 7001 almost the same (3.35, 3.34 and 3.35 eV, respectively). On the other side the powders differ in the presence of doping phase which was determined only for vlp7000 ($E_g = 1.85$ eV) and vlp7001 ($E_g = 1.83$ eV).

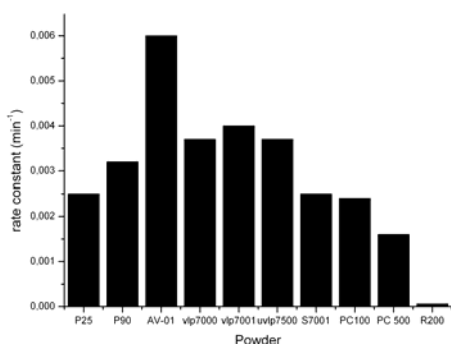


Figure 1

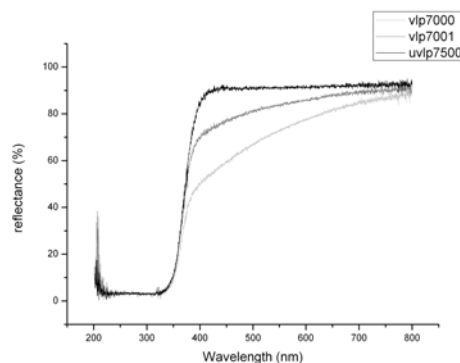


Figure 2

Acknowledgements

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**DEVELOPMENT OF CAPACITIES IN CATHODE
OLIVINE/CARBON NANO-COMPOSITE MATERIALS**MILAN BOUŠA^{a,b,*}, OTAKAR FRANK^a AND LADISLAV KAVAN^a^a*J. Heyrovský Institute of Physical Chemistry, v.v.i.,
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Lithium-ion batteries are widely used as power sources in many devices and are expected as a source of energy in electric vehicles. Electrochemical qualities of lithium-ion batteries depend on variable factors like physical and chemical properties of electrode materials. However, it is necessary to prepare safe materials with low cost but with sufficient power/energy density.

In this work we used mainly nanocrystalline LiFePO₄ olivine-type material (LFP) as the cathode material because of its low-cost, stability and availability. To improve the conductivity and charge transfer in the active electrode material, some form of sp²-hybridized carbon should be added. In the presented study we compare carbon nanotubes, conductive carbon black and few-layer graphene oxide (FLGO) as the additive to olivine material. Various voltametric and amperometric measurements were performed to investigate the influence of the carbon material on the reversibility, cycle stability and capacity of the prepared electrodes.

The composite of LFP and FLGO shows an intriguing evolution of capacities during the electrochemical cycling. To elucidate the observed behavior, Raman and IR spectroscopy were used for the characterization of the structural changes in the graphene oxide induced by electrochemical charge/discharge processes.

PRISTINE FULLERENE C₆₀ IN AQUEOUS MEDIUM

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Promising applications of fullerene in the fields of material sciences, catalysis and especially medicine have their limitation in the solubility of this molecule in water environment. Therefore, several strategies were undertaken to overcome this problem. The complexation of C₆₀ with organic host molecules is probably the most common method [1]. Other possibility is the chemical derivatization of C₆₀. Recently, sonication was applied to a two-phase mixture of toluene containing C₆₀ and water without any stabilizer until the evaporation of toluene was completed [2]. The dispersion of C₆₀ in water was obtained. The problem of stability of C₆₀ aggregates in aqueous medium have been the subject of several recent studies [2,3,4].

In this contribution we are interested in behaviour of pristine fullerene C₆₀ in aqueous medium. Stable aqueous colloidal dispersions of fullerene C₆₀ were analysed by electrochemical and spectroscopic methods, by TOF-SIMS, MALDI-MS, ESI-MS, LCMS, Dynamic Light Scattering and by AFM/STM techniques. Present communication will present mainly the AFM/STM techniques. Most of mentioned methods confirmed that C₆₀ clusters are stabilized in the aqueous solution by the presence of thin layer of benzoate derivatives produced during sonication [5].

Acknowledgement

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DIFFERENT METHODS FOR PYRITE FeS_2 THIN FILMS— — A POTENTIAL SOLAR CELL MATERIAL

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On the basis of material extraction costs leading to significantly lower cost per kilowatt-hour, FeS_2 is the most promising material for photovoltaic applications. Although this material has not been studied extensively, its potential for use in photovoltaics has been explored. The material has a very high absorption coefficient, $\alpha \geq 5 \times 10^5 \text{ cm}^{-1}$ for $\lambda \leq 700$ with hole mobilities in the order of $100 \text{ cm}^2/\text{Vs}$.

Thin pyrite films were prepared by sulfurizing the iron oxide films previously deposited through a catalyzed sol-gel method using iron (III) chloride as a precursor. Further a simple chemical bath deposition (CBD) for the preparation of iron disulfide (pyrite, FeS_2) thin films have been studied using $\text{Fe}(\text{NO}_3)_3$ and $\text{Na}_2\text{S}_2\text{O}_3$ as sources of Fe and S, respectively and disodium ethylene diamine tetra acetic acid ($\text{Na}_2\text{-EDTA}$) as the complexing agent. The complexing agent is the most important component of the chemical bath because it greatly influenced the structural and electro-optical properties of the thin film. Finally, magnetron sputtering of pure iron followed by chemical sulfurization to produce pyrite was also performed. The structural, morphological and optical properties of the deposited films have been studied using x-ray diffraction, Raman spectroscopy, scanning electron microscopy, Auger electron spectroscopy, UV-Vis absorption spectroscopy and profilometry.

Fig. 1 shows the Raman spectrum of the sol-gel $\alpha\text{-Fe}_2\text{O}_3$ (hematite) coating after sulfurization at different temperatures. Using the temperature of $450 \text{ }^\circ\text{C}$ led to the chemical sulfurization of hematite phase film to pyrite FeS_2 . The surface of the pyrite film deposited through the CBD method and sulfurized at $450 \text{ }^\circ\text{C}$ for 1 hr appeared homogeneous with a smooth morphology (Fig. 2).

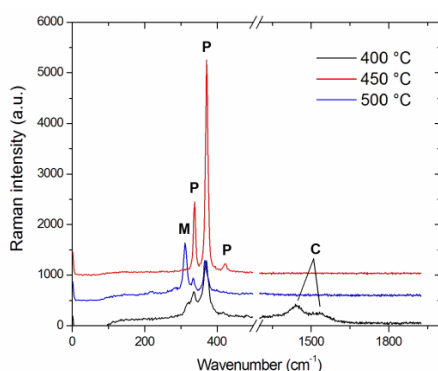


Figure 1

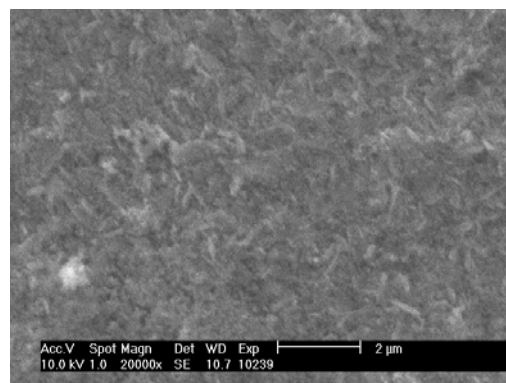


Figure 2

ADSORPTION OF N719 DYE ON MESOPOROUS TiO₂ FILMS CONTAINING TiO₂ NANOFIBRES

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The mesostructured electrodes for dye-sensitized solar cells (DSSC) are generally fabricated from TiO₂ sol-gel processed sintered nanoparticles. These films are highly porous (about 60%) and deliver a surface area multiplicity of around 1000 in a ten micrometer thick film [1], necessary for sufficient sensitizer loading to achieve high current density. TiO₂ nanofibres can provide interlinking between nanoparticles and improve the efficiency of electron transport towards the transparent conducting oxide electrode, reducing the time available for recombination with holes. The aim of our work was the investigation of the effect of fibrous TiO₂ incorporation into the TiO₂ mesoporous structure on the adsorption of N719 dye. The higher dye adsorption the more effective electron transport from dye to the mesoporous film and consequently the efficiency of solar cell is higher.

Titanium dioxide films were grown by implementing the protocol of supramolecular templating with an amphiphilic triblock copolymer, Pluronic P123 [2] stabilized with phosphorus [3] and by mixing with TiO₂ nanofibers. Thin mesoporous films were prepared via layer-by-layer deposition applying dip coating. Deposition of each layer was followed by thermal treatment at 350°C for two hours [3,4].

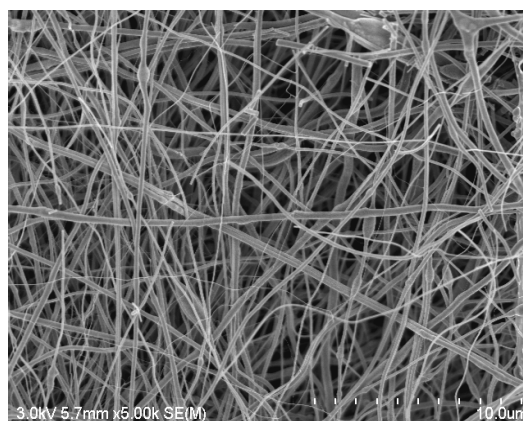


Figure 1: Electrospun TiO₂ fiber structure

Acknowledgements

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PAPAIN ADSORPTION ON THE MODIFIED ELECTRODE SURFACES OF DIFFERENT DEGREE OF HYDROPHILICITY – AN AFM STUDY

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Papain (EC 3.4.22.2, papaya proteinase I) is a cysteine endopeptidase in latex of the Papaya tree (*Carica papaya*, Caricaceae). The protein has 212 aminoacids and molecular mass 23 kDa. Papain consists of a single polypeptide chain with three disulfide bridges and a sulphhydryl group in the active site. [1] This free SH group of Cys25 could be modified by covalent binding with the organometallic complexes. The artificial metalloenzymes, which are produced by this modification, could have new catalytic activity (e.g. Diels-Alder cycloaddition, hydrogenation, transamination etc.). [2] In our recent work papain was modified by the organometallic fragments of the general type $[(\eta^6\text{-C}_6\text{H}_5(\text{CH}_2)_2\text{NHCO}(\text{CH}_2)\text{Cl})\text{Ru}(\text{N}^-\text{N})\text{Cl}]\text{Cl}$ and the electrocatalytic properties of such biomolecules have been studied in aqueous environment. It has been shown that the electrochemistry of modified papain is influenced by its adsorption on the electrode surface. Therefore, the aim of this contribution is to explore the adsorption properties of papain at substrates with different hydrophilicity by AFM measurement [3].

Papain adsorption was studied at highly oriented pyrolytic graphite (HOPG), at bare single crystalline gold(111) electrode and after modification of the gold(111) substrate with different alkanethiol monolayers. Character of the protein layer was studied using the intermittent contact mode and contact mode scratching, respectively.

A submonolayer of protein was found on the hydrophobic HOPG surface, similar result was obtained on the gold(111) modified by 1-dodecanethiol. Papain forms a compact monolayer on the gold(111) substrate covered by 11-mercaptoundecanoic acid monolayer. After modification of gold(111) by 11-mercapto-1-undecanol protein forms a multilayer structure, which was also confirmed by the statistical analysis of the layer thickness after the application of contact mode AFM scratching. This work shows that the hydrophilic surface containing COOH-terminated interface is the most suitable for the reproducible preparation of papain monomolecular films on the modified electrode surfaces.

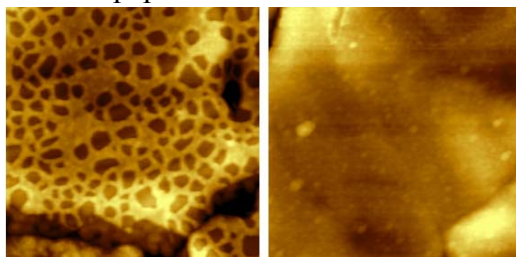


Figure : Layer of papain on gold(111) modified by 1-dodecanethiol (left) and by 11-mercaptoundecanoic acid (right)

Acknowledgements

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SPECTROELECTROCHEMICAL INVESTIGATION OF (001)-ORIENTED ANATASE TiO₂ NANOSHEETS

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TiO₂ anatase is an attractive material for applications in photoelectrochemical solar cells. The thermodynamically most stable is TiO₂ anatase with dominating (101) face followed by (001) and (100) faces. However, recently favourable properties of (001)-oriented anatase with respect to its application in Li-ion batteries and dye sensitised solar cells have been published¹. The spectroelectrochemical behavior of polycrystalline TiO₂ anatase with a predominant (001) face was studied and compared to a reference anatase material with dominating (101) face. Transparent nanostructured TiO₂ films were prepared and UV/Vis spectroelectrochemistry at potentials between 0 and -1.4V was used to determine the flatband potentials. Optical absorption spectra proved negative shift of flatband potential for (001) anatase as compared to (101) one. This different band energetic point at larger open circuit voltage of the solar cell with using (001) anatase electrode as a photoanode.

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REDOX PROPERTIES OF IMIDAZOLE BASED TUNABLE CHROMOPHORES FOR NON-LINEAR OPTICS

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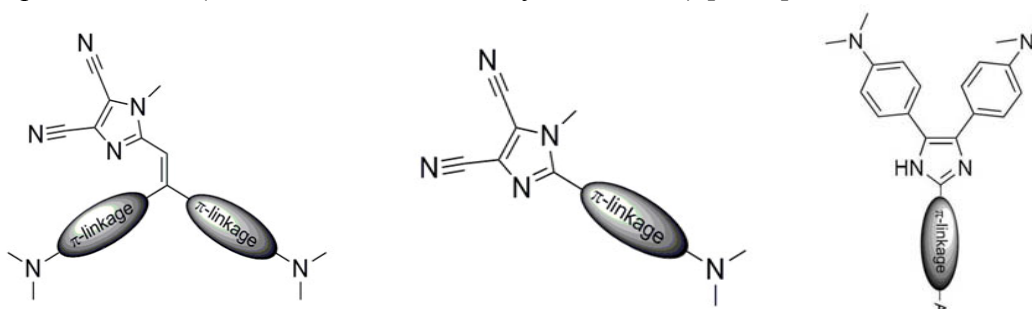
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Imidazole based molecules bearing electron donating and electron withdrawing centers, that are connected by a systematically extended π -conjugated bridging system are attractive as tunable chromophores for nonlinear optics (NLO). Their broad application involves e.g. two-photon absorbing devices, opto-electronic and optical data storage devices, organic light-emitting diodes (OLED) or organic photovoltaic cells. Recently, several new series of imidazole derivatives (about 50 compounds) were synthesized with NO₂ or CN groups as strong electron acceptors - A and NR₂ or OR groups as donors - D [1]. Such an organic D- π -A chromophore represents a typical "push-pull" system.

The new compounds were electrochemically characterized by polarography, cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile, N,N-dimethylformamide) [2,3,4].



Though the molecules exhibit several redox processes, from the aspect of NLO, the attention has been paid mainly to the first oxidation and first reduction step that should be reversible, involving one transferred electron. The influence of the imidazole core and different linker has been followed and a mixed influence of length and planarity was found and discussed. The most suitable chemical compositions were selected and the more general rules concerning the influence of individual building blocks was formulated.

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THIN FUNCTIONAL FILMS OF TiO₂ NANOPARTICLES

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Most of the semiconductor thin layers practically employed as photoactive electrodes reveal very low extent of characteristic (periodic) structural features. They are composed of arrays of pores of various shapes, sizes and volumes, mixed crystallographic phases, etc. and phenomena associated with their functions take place on surfaces containing physical (e.g. pits, ridges) and chemical (e.g. polar sites) defects. However, it is possible to produce very uniform, organized structures finalized as thin layers and exhibiting unique properties and functions. Here we report on preparation of titanium (IV) oxide nanoparticulate thin films by a series of methods. Physical methods include Barrier-torch Discharge deposition, Magnetron Sputtering and the Modulated Hollow Cathode Plasma Jet Sputtering. As chemical method the sol-gel process carried out in the templating environment as dip-coating and piezo-jet printing was employed. The produced films differed in many structural characteristics and also in their photoelectrochemical behaviour, as the primary sought function. The produced layers were described by means of atomic force microscopy, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, ultraviolet-visible spectroscopy, Raman spectroscopy, ellipsometry and profilometry. Then the films were used as electrodes in photoelectrochemical experiments.

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OPTICAL CHARACTERISATION STUDIES OF NOVEL DIKETO-PYRROLO-PYRROLES

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Introduction

In order to study the influence of end structures added to form chromophore derivatives for the purpose of organic light emitting compounds one should go through the study of several optical processes. Diphenyl-diketo-pyrrolopyrrole (DPP) as newly synthesized possible chromophores are of a great interest for our research group [1,2]. Due to their interesting properties, they have been already investigated covering for example latent pigment, charge generating materials for laser printers, information storage systems and solid-state dye lasers or gas detectors. One and two photon absorption like amplified spontaneous emission measurement techniques were conducted for the optical study of prepared derivatives.

Results and discussion

The introduction of alkyl groups (also functionalised) at R3 and R4 ends of DPP core helped with their solubility. This was an important goal to achieve for the making of thin layers films throughout simple spin coating procedure. Keeping R3 and R4 identical allowed us to afford unsymmetrical DPPs by interchanging different substituents R1 and R2. They were of different types whether with electron withdrawing or electro donating groups resulting in a permanent dipole. Several optical processes were studied like the amplified spontaneous emission of some DPPs derivatives. As for, the pigments were doped in polymer and its thin layers were then pumped with third harmonic generation (THG, 355nm) produced by a Nd:YAG picoseconds pulsed laser. By narrowing the shape of the incident laser beam perpendicularly on the thin layer and increasing its energy, one could analyze the out coming energy from the sample waveguide's edge and observe the narrowing of the emission spectra corresponding to "superluminescence". Amplified spontaneous emission [3] spectra were obtained by doping certain polymer with a DPP. The choice of the polymer which had to be chemically passive was crucial for the stability of this particular effect. We still must define the different processes involved in this optical mechanism and therefore some advanced studies and interpretation must be overcome to consider the prior reason for the effect.

The one and two photon emission spectra measurement were obtained by the search of the precise and appropriate concentration of the samples. This was needed to be tested and found according to the incoming laser beam energy to be able to get significant results avoiding reabsorption or diffusion effects on the molecules when excited.

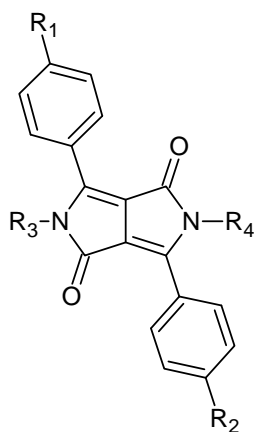


Figure 1: The basic structure of 3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4 dione, also known as DPP derivatives.

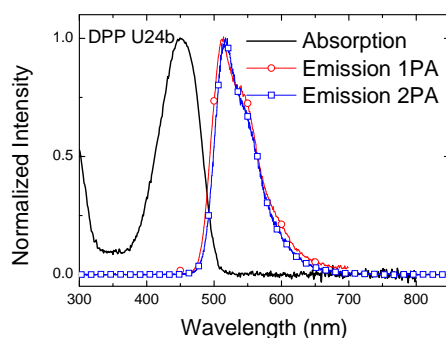


Figure 2: Absorption and 1 and 2 photon emission (1PE and 2PE) spectra of a single DPP derivative

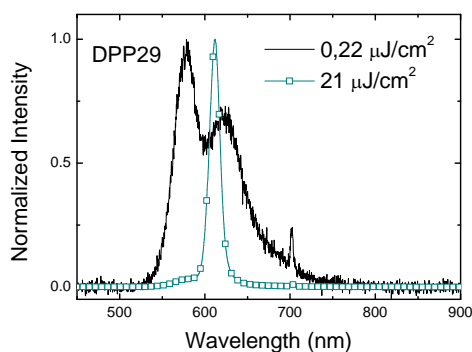


Figure 3: Amplified spontaneous emission demonstrated for DPP (29) derivative.

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THE ELECTROCHEMICAL STUDY OF MONOLAYERS OF ORGANOSTANNYL DERIVATIVES ON GOLD SURFACE

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Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) are suitable techniques for the monitoring of the changes in electron transfer of redox probes in the presence of the self-assembled monolayers (SAMs). The monolayers can be grown by chemisorptions on different substrates such as Pt, Pd, Au, Ag, Cu, etc., to form a highly ordered surface. These composites are widely used as sensor, nonlinear optical materials, molecular electronics, corrosion inhibitors, etc.[1, 2] Nevertheless, SAMs of organothiols on gold which are exposed to air slowly undergoes to oxidation and the relatively poor electronic communication through the electronegative sulfur atom restrict their use in certain applications for example in molecular electronics. It is desirable to find alternative modes of single-molecule attachment to metal surfaces and the electropositive nature of the ligand atom might be favorable for electronic communication. The present work follows up on observation of the adsorption of organomercuryl and organostannyl cations on gold, accompanied by the loss of the trifluoroacetate, tosylate and triflate anion.[3, 4]

In this work, we present an electrochemical study of the Sn-SAMs spontaneously formed on a glass substrate coated with 200 nm of gold. We investigated the electrochemical blocking properties and stability of organostannyl monolayers. Sn-SAMs were prepared by immersing of the gold substrate in solution of an appropriate agent for 2 h. After removal from solution, the composites were rinsed three times with pure solvent and dried under a stream of nitrogen prior to analysis. Obtained results were compared with previously studies of organomercuryl and organothiols monolayers. Samples were characterized by using a home-built three-electrode system for the CV and EIS. A gold substrate (either clean or carrying an adsorbed layer), a platinum wire, and an Ag/AgCl electrode were used as the working, auxiliary, and reference electrodes, respectively. This study confirms that alkylstannyl derivatives are suitable alternatives to thiols in specific modification of metallic electrode surface.

Acknowledgement

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CHARACTERIZATION AND STABILITY OF NANOPARTICLE ELECTRODES

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The formation and properties of single-component nanoparticle assemblies of Pt, Pd, Au, Ni, Cr and Mn, each having significance in (electro)catalytic/charge storage processes were examined. Multilayer graphene (basal plane highly ordered pyrolytic graphite, HOPG) served as a collector-support for nanoparticle assembly deployment. Complex characterization by composition (X-ray photoelectron spectroscopy, XPS), nanomorphology (atomic force microscopy, AFM), electron conductivity (scanning tunneling microscopy, STM and spreading resistance AFM respectively) and by feasibility of charge transfer (cyclic voltammetry) was performed. The assembly stability was evaluated from XPS analysis and quantitative charge transfer reproducibility respectively. The stability of nanoparticle assembly at the solid/liquid interface was found to be closely linked to the chemical composition, reaction conditions and path, while deposition technique did not play a significant role. The stability was found to reach maxima for oxide and oxo-hydroxide anionic paths in which, besides their dissociation limits, the metal oxide-graphene interaction plays the stabilizing role. Transitions via metallic and cationic form accompanied often by complexation and parasitic gas nanobubble formation respectively, led to irreversible decay from the assembly. The finding brings the stability of nanoparticle deployment as a key issue in commercial utilization and points to optimization of reaction conditions not only with respect to mediated process but also with respect to catalyst deployment stability.

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**SPONTANEOUS ACTIVATION AND SUBSEQUENT ANODIZATION
IN AQUEOUS SOLUTIONS OF TITANIUM ELECTRODES
IN CONDITION LEADING TO OSCILLATORY MODE**

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Recently we have disclosed and published [1] very special case of titanium anodization characterized by current oscillations under potential control. For this to be achieved, the Ti electrode has to be activated in solution containing fluoride ions. Oscillations have a relaxation character similar to glow discharge in gas. We presume important applications of oscillatory mode of Ti anodization, analogously to similar oscillations on Si, recognized, broadly described and successfully applied [2].

Reference

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IN-SITU RAMAN SPECTROELECTROCHEMICAL CHARACTERIZATION OF BORON-DOPED NANOCRYSTALLINE DIAMOND (B-NCD)

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Boron-doped diamond thin films (p-type conduction) have recently appeared as a new promising unique electrochemical material due to its extreme and beneficial properties such as mechanical hardness, chemical inertness, wide potential window, excellent stability, reproducibility and controlled conductivity, depending on the electrode doping level, morphology and microstructure [1].

In this work we report especially on *in-situ* Raman spectroelectrochemical measurements of boron-doped nanocrystalline diamond (B-NCD) which allow to monitor structural (electronic, phase) changes during different potential applied. Diamond thin films were grown by hot-filament chemical vapor deposition and doped with various boron concentrations in the range from 500 to 6000 ppm (B/C ratio in the gas phase). First of all, the quality (presence of graphitic or amorphous phase) and boron doping levels in the B-NCD films have been analyzed by Raman microscopy, followed by cyclic voltammetry (CV) measurements. In the Raman spectra differences can be observed, owing to a different boron content in the prepared films. As the boron concentration increases, bands corresponding to the boron doping (Fano effect) start to appear at around 500, 1000 and 1200 cm⁻¹ [2] and at the same time the characteristic line for diamond (sp³ carbon) at 1332 cm⁻¹ downshifts and its intensity decreases. Raman spectra have exhibited also a sp² carbon (E_{2g} - "tangential") peak around 1580 cm⁻¹. The electrochemical potential window depends especially on the film quality, i.e. on the amount of the graphitic phase present on the B-NCD grain boundaries. As the sp² carbon content increases, the potential window of the films decreases from usual values for pure B-NCD films (i.e. only diamond sp³ phase). The *in-situ* Raman spectroelectrochemistry has been performed in aqueous electrolyte (1M KCl) in the potential range of approximately -1.5 to 1.5 V vs. Ag/AgCl with potential step of 0.25 V. The modes belonging to both sp³ and sp² carbonaceous phases change their positions and intensities. For example, the main sp³ (diamond) peak redshifts and its intensity increases with increasing potential. The sp² tangential mode experiences a similar evolution, however, the exact rates of intensity and position changes with potential are slightly different to those of sp³ diamond peak.

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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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