Programme and Book of Abstracts

SMCBS'2011

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Published October 2011, ISBN 83-89585-32-4

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Cover design and photo: Martin Jönsson-Niedziółka
Revision: 43.0.57, 2011-10-27 20:14 GMT

Table of Contents

Welcome

We are pleased to present this programme of the 5th International Workshop on Surface Modification for Chemical and Biochemical Sensing, SMCBS, organised by The Polish Supramolecular Chemistry Network Foundation under the auspices of the Institute of Physical Chemistry, Polish Academy of Sciences. In the spirit of the previous meetings we are especially happy to see so many contributions from young researchers who present their results in short oral communications or in the form of posters. We are also proud that over a dozen distinguished scientists have accepted our invitations to deliver tutorial lectures that can function as the basis for further discussions.

With an increasingly complex chemical environment, the development of new chemo- and biosensors is a vital tool for monitoring the ecosystem, safeguarding our food supply and providing crucial information for clinical diagnosis and therapy. As the trend goes towards both increasing sensitivity and selectivity control over the specific properties of the sensor surface becomes all the more important. The development of modern sophisticated chemo- and biosensors requires collaboration not only from the fields of chemistry and biology, but also from physics, materials science, electronics, etc. Although the centre of gravity of the SMCBS workshops continues to be on the electrochemical aspects of sensing, we hope that the broad spectrum of participants can nurture the interdisciplinary meetings that give rise to new important ideas.

As with the previous meetings in the SMCBS series, organised in Białowieża (2003), Kazimierz Dolny (2005), Włodowice (2007), and Przegorzały (2009), this year's workshop hosts all the participants in a single location to give ample opportunity for researchers to meet for discussions and exchange of ideas that might lead to new research concepts and, most desirably, mutual collaborations.

The Organising and Programme Committee is grateful to all those who contributed to the present workshop. We are particularly thankful to the authors of the contributions, to the persons chairing the sessions and the members of the International Scientific Advisory Board.

On behalf of the Organising and Programme Committee we welcome all the participants and wish you an excellent workshop, both scientifically and socially.

Włodzimierz Kutner and Marcin Opałło
Warsaw, Oct 2011

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Programme

Friday, 4 November

Arrivals and registration
Friday afternoon, 4 November, 15:00

Dinner
Friday evening, 4 November, 19:00

Saturday, 5 November

Breakfast
Saturday morning, 5 November, 8:00

Introduction and Welcome
Saturday morning, 5 November, 9:00

Morning Session 1
Saturday morning, 5 November, 9:10
Chair: Jeuken and Plumeré

9:10 Tutorial lectore

Research and Development of Enzyme based Electrochemical Biosensors. The case study of nitrite biosensing.

Maria Gabriela Almeida

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The last few decades have witnessed a steady increase of the social and political awareness for the need of monitoring and controlling numerous agricultural, environmental and industrial activities. Consequently, the most important governmental agencies have promulgated rules and directives to restrict the level of many chemical compounds in waters, foodstuff and industrial products. Worldwide legislation is thus driving the development of novel and highly efficient analytical tools. Clinical diagnostics and research in biomedical sciences are also demanding optimal sensors tailored for the specific needs of real-time measurements either in vitro or in vivo [1].

The fast-growing biosensor technology is one of the most active R&D domains of Analytical Sciences focused on the challenge of taking analytical chemistry to the field. Electrochemical biosensors based on redox enzymes, in particular, are highly appealing due to their usual quick response, high selectivity and sensitivity. In addition, they are cost-effective and easy to fabricate in portable dimensions. However, the implementation of these biosensorial systems may face several obstacles. Once chosen the enzyme candidate for the specific recognition of a target analyte, it should be efficiently immobilized atop the electrode surface, minimizing protein leakage and denaturation. Also,

the immobilization matrix should work as a barrier against fouling and interfering species and, more importantly, should guarantee an efficient electronic communication between the redox sites of the protein and the transducing platform. Therefore, surface modification of electrodes plays a critical role on the construction of enzyme based electrochemical biosensors [1].

This communication aims to provide an overview of the many different strategies lately proposed to overcome the setbacks above mentioned. The pros and cons of some of these approaches will be illustrated through the case study of nitrite biosensors based on redox enzymes with catalytic activity for this analyte. In fact, our group has proposed a variety of routes for the construction of nitrite biosensors using the fast and robust cytochrome *c* nitrite reductase from *Desulfovibrio desulfuricans*, which catalyzes the reduction of NO_2^- to NH_4^+. Fully integrated bioelectrodes including synthetic redox mediators combined with a variety of immobilization were initially proposed [2-4]. More advanced strategies operating through direct electron transfer [5] and exploiting nanostructured materials [6,7] were subsequently reported. Very recently, we have also proposed a novel biosensor based on cyt. cd_1 nitrite reductase (converts NO_2^- into NO), which was successfully co-entrapped with its physiological redox partner, the electroactive cyt. c_{552} [8], indicating that the cooperative use of enzymes and their physiological redox partners could become a new trend in the design of electrochemical biosensors.

References: [1] M.G. Almeida et al., *Sensors* **2010**, 10, 11530; [2] M.G. Almeida et al. *Biosens. Bioelectron.***2007**, *22*, 2485; [3] S. Silva et al. *Electrochem. Commun*. **2004**, *6*, 404; [4] H. Chen et al., *Electrochem. Commun.***2007**, *9*, 2241; [5] Silveira et al. *Biosens. Bioelectron.***2010**, *25*, 2026; [6] C. Silveira et al. *Electroanalysis***2010**, 22, 2973; [7] C. Silveira et al., *in preparation*; [8] A.S. Serra et al**.** *Anal. Chim. Acta,***2011***,693,* 41-46.

9:50 Keynote lecture

Electrochemical biosensors: Gelatin as a biocompatible matrix for the incorporation of redox enzymes

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The incorporation of enzymes in hydrogels, adsorbed to electrode surfaces, is a promising research line in the field of bioelectrochemistry. In this work, gelatin is selected as hydrogel for the encapsulation of different redox enzymes [1-2]. Gelatin is a water soluble protein, composed of a variety of amino acids, via amide bonds form a linear polymer with a molecular weight between 15000 and 250000 Da [3]. Due to the hydrophilic groups or domains, the hydration and native configuration of the encapsulated biomolecules is ensured. The entrapment of enzymes in a hydrogel without a membrane results in a faster response or a faster diffusion of analyte to the enzyme. In addition, an increased enzyme stability is obtained next to a better resistance to dehydratation/rehydratation which has his benefits concerning the storage of the biosensor.

In the present work, we compare different strategies to immobilize gelatin layers on electrode surfaces: drop dried and spincoated layers. Within the gelatin matrix, we can encapsulate different enzymes such as horse heart cytochrome *c* [3], cytochrome *c* peroxidase, catalase, … Depending on the selected immobilization method, we observe different electrochemical behaviour of the immobilized enzymes. Additionally, the electrocatalytic behaviour of the enzymes towards their target molecules is investigated. Our strategy is to create an open hydrogel for the predictable response of quasi-freely diffusing enzyme, mediator and substrate (analyte). This method is now a model system for new biosensor applications in industry.

[1] K. De Wael, S. De Belder, S. Van Vlierberghe, G. Van Steenberge, P. Dubruel, A. Adriaens, Talanta 82(5) (2010) 1980-1985.

[2] K. De Wael, B. Qamar, S. Van Vlierberghe, P. Dubruel, H. Heering, A. Adriaens, Bioelectrochemistry, in press

[3] J.E. Eastoe, A. A. Leach, in ‘The science and technology of gelatin’, (Eds. Ward A.G., Courts A.), Academic Press, New York (1977) Chapter 3.

10:10 Short communication

Design of a highly sensitive electrochemical biosensor for methyl mercaptan detection

Zhanhong Li[1,2], Houssemeddine Guedri[1], Bruno Viguier[1], Shigang Sun[2], Jean-Louis Marty[1]

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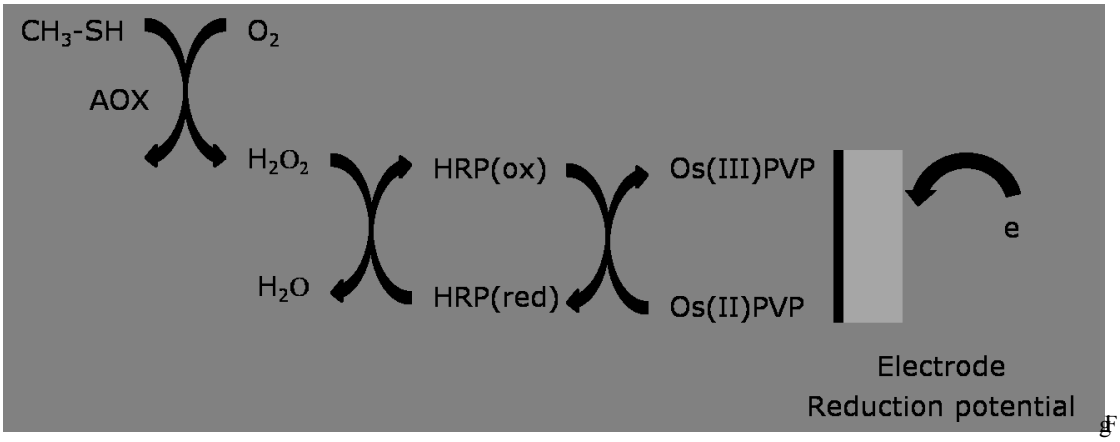
Methyl mercaptan (MM) is mostly known because it is the predominant volatile organic compounds (VOCs) involved in halitosis (bad breath). Detection of MM in breath can also evaluate liver damage and hepatic coma.

In this work, a highly sensitive electrochemical biosensor for MM detection was developed. This biosensor is based on the enzymatic reaction between the MM and the oxygen (O_2) to form hydrogen peroxide (H_2O_2) (Fig. 1). This reaction is catalyzed by alcohol oxidase (AOX). The immobilization of enzyme was cross-linked by BSA and glutaraldehyde on carbon screen-printed electrode (SPE). Working electrode was first modified by osmium wired HRP (Os-HRP) and electrochemical measurements were performed in phosphate buffer at a working potential of -100mV versus Ag/AgCl. The AOX biosensor showed a low detection limit of 0.5 mM compared to other work [1].

In future work, the biosensor will be applied to detect gaseous MM as a bio-sniffer with a reaction unit having liquid–gaseous compartments separated by a hydrophobic porous polytetrafluoroethylene (PTFE) diaphragm membrane.

Financial support from MEDISEN project is gratefully acknowledged.



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1: Principle of methyl mercaptan measurement using AOX enzymatic reaction and Os-HRP

1. Minamide, T., K. Mitsubayashi, and H. Saito, *Sensors and Actuators B: Chemical*, **2005**. *108(1-2)*: p. 639-645.

10:25 Short communication

Novel platform for electrochemical sensors and biosensors based on on-chip functionalized vertically aligned carbon nanotubes

Wolfgang Harreither[1], Waqas Khalid[2,3], Johan Dunevall[1], Bengt Norden[2], Andrew G. Ewing[1,2], Gulnara Safina[1]

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Vertically aligned carbon nanotubes (VA-CNTs) have attracted the attention of researches in recent years due to their unique physical properties. The extraordinary electrical properties of carbon nanotubes, the porous nature and the large surface area of their 3D structures combined with the ability to synthesize them in relatively controlled fashion have open up new possibilities of using them as an excellent nanomaterial to develop electrodes for analytical sensing devices. In comparison to the conventional 2D microelectrodes, such 3D structures provide a very large and developed surface area, excellent for detection of low concentrations of biomolecules with higher signal-to-noise ratio. Functionalization of the surface of VA-CNTs brings new additional possibilities to develop sensitive and highly specific miniaturized chemical sensors and biosensors. In this work we applied a novel technology in the synthesis of VA-CNT. Metal catalyst (Fe) was used to grow VA-CNTs on a chip. In contrast to many existing chip fabrication technologies, metal was used as a buffer layer between the substrate and the catalyst. This resulted in an excellent electrical conductivity of the VA-CNTs. The height of the VA-CNTs grown on a chip varies from a few hundreds μm to 1 mm. We demonstrate that the electrochemical pre-treatment of the electrode surface led to the improved analytical signal obtained from the tested electrochemical species (ferrocyanide, ferrocene methanol and dopamine). VA-CNTs were functionalized with cellobiose dehydrogenase from Neurospora crassa (NcCDH) by a simple physical adsorption of the enzyme on the chip surface. NcCDH is capable of transfer the reaction electrons from oxidizing mono- and disaccharides to electrodes without the need of mediators. We demonstrated that VA-CNTs, in contrast to other electrode materials, showed an improved direct electron transfer between the immobilized enzyme and the electrode surface. The catalytic current was clearly observed in the presence of substrate starting from -100 mV vs. Ag/AgCl electrode. The experiments have shown that the chip is reusable, i.e. multiple immobilizations of the fresh portions of the enzyme do not deteriorate the working features of VA-CNTs. Different VA-CNTs based working surfaces (hydrophilic, hydrophobic) were tested with respect to their capabilities to adsorb the enzyme and keep its catalytic properties. The surface of the functionalized nanotubes on a chip was investigated using SEM and EDX. The chip may be integrated in a flow cell or microfluidic system. Further, modification of the VA-CNTs with other molecules is under progress. The preliminary data that we obtained demonstrate that on chip functionalized VA-CNTs are excellent and versatile platform for construction of electrochemical sensors and biosensors.

Coffee Break

Saturday morning, 5 November, 10:40

Morning Session 2

Saturday morning, 5 November, 11:00

Chair: Almeida and Safina

11:00 Tutorial lectore

Electrodes for integral membrane enzymes

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Redox proteins and enzymes are involved in a large number of processes mainly related to bioenergetic metabolism or photosynthesis. Many of the enzymes are oxidoreductases and an important group of them reside in bacterial, mitochondrial or chloroplast (inner) membranes. In the eighties, reports emerged in which redox proteins and enzymes are immobilised on 'protein-friendly' electrode surfaces while electrons are exchanged between the protein and electrode. Since then, hundreds of papers have appeared in which electrochemistry is used to study redox proteins and the catalytic mechanisms of redox enzymes. As so often in protein biochemistry, the field has made significantly less progress with membrane proteins than with globular proteins. In this tutorial lecture I will focus on focus on integral membrane oxidoreductases and provide an overview of the strategies used to make electrodes suitable for membrane proteins. This lecture will discuss various technologies that have been used to immobilise enzymes on the electrode surface and to 'coach' them to exchange electrons, either directly or with the help of mediators.

11:40 Keynote lecture

Fully active enzyme monolayers on electrode surfaces – Control of spatial distribution and protein orientation.

Nicolas Plumeré

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This lecture focusses on several challenges in self-assembled monolayers of redox enzymes on electrode material surfaces. Strategies to immobilize the enzyme in its active form will be presented first. Electrode surface functionalization with metal complexes is designed to afford a stable binding via histidine residues from the enzyme surface. The electrocatalytic enzyme activity is preserved when an electron mediator is used for the charge transfer with the electrode.

Direct electrochemistry of the redox enzyme is even more attractive for mechanistic studies, biofuel cell or biosensing applications. The direct electron transfer requires a short distance between the redox center of the enzyme and the electrode surface. Therefore, for optimized direct electron transfer, the orientation of the redox enzyme must be controlled to bring the redox center in the appropriate position with respect to the electrode surface. Our strategies involve the introduction of both natural and unnatural amino acids at the surface of the protein in the desired location for the binding site. Immobilization is achieved by affinity binding or covalent linkage.

For multiple analytes sensing, multiple biorecognition elements must be spatially separated and individually addressed. Toward SECM and electrode array based patterning applications, an electrochemically cleavable protecting group for protein anchoring sites was developed. The surface modification procedure is possible without introducing any coupling reagents and can therefore be seen as a true local patterning procedure.

In the last part, an approach to prevent oxygen interference in field application of biosensing devices will be presented.

12:00 Short communication

Nitrite Reductase, an enzyme for which kinetics are different at rest than during turn over.

Lukasz Krzeminski[1], Lionel Ndamba[2], Gerard W. Canters[2], Thijs J. Aartsma[2], Stephen D. Evans[1], Lars Jeuken[1]

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A combined fluorescence and electrochemical method is described that is used to simultaneously monitor the type-1 copper oxidation state and the nitrite turn-over rate of a nitrite reductase (NiR) from *Alcaligenes faecalis* S-6. The catalytic activity of NiR is measured electrochemically by exploiting a *direct* electron transfer to fluorescently labeled enzyme molecules immobilized on modified gold electrodes, whereas the redox state of the type-1 copper site is determined from fluorescence intensity changes caused by Förster Resonance Energy Transfer (FRET) between a fluorophore attached to NiR and its type-1 copper site. The homotrimeric structure of the enzyme is reflected in heterogeneous interfacial electron transfer kinetics with two monomers having a 25-fold slower kinetics than the third monomer. The intramolecular electron transfer rate between the type-1 and type-2 copper site changes at high nitrite concentration (≥520 mM) resulting in an inhibition effect at low pH and catalytic gain in enzyme activity at high pH. We propose that the intramolecular rate is significantly reduced in turn-over conditions compared to the enzyme at rest, with an exception at low pH / nitrite conditions. This effect is attributed to slower reduction rate of type-2 copper centre due to a rate-limiting protonation step of residues in the enzyme's active site, gating the intramolecular electron transfer.

12:15 Short communication

Influence of metal cations on the turnover rate of cellobiose dehydrogenase

Christopher Schulz[1], Roland Ludwig[2], Lo Gorton[1]

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Cellobiose dehydrogenase (EC 1.1.99.18) is an extracellular fungal redox enzyme, which has recently shown promising properties for applications in both biosensors and biofuel cells [1]. It is a two domain enzyme composed of a catalytic FAD containing domain connected through a polypeptide linker region with a cytochrome *b* domain. In the catalytic reaction, the substrate is oxidised at the FAD domain, which in turn is reoxidised through an intramolecular and sequential electron transfer process donating the electrons to the cytochrome *b* domain, from which the electrons can be donated directly to an electrode. The mechanism with which the electrons are transferred between the two domains is unknown and very pH dependent. However, it is believed that the surface exposed heme of the cytochrome *b* domain enters the substrate channel of the FAD domain allowing the electrons to be transferred between the two domains.

We have now found that when increasing the concentration of metal cations the rate of the intramolecular electron transfer reaction of CDH immobilized on an electrode surface could be increased substantially up to 23 times. Increases were higher with divalent metal cations compared to monovalent metal cations, but were also dependent on the type of cation, confirmed also by enzymatic assays of CDH in solution. These findings are of interest both for a deeper understanding of the electron transfer pathway in the enzyme and a way how to increase the bioelectrocatalytic current density when the enzyme is used in the direct electron transfer mode on an electrode. Recent results and a proposed mechanism to explain the observed effect will be shown and discussed.

References:

[1] R. Ludwig, W. Harreither, F. Tasca, L. Gorton; *ChemPhysChem*, **2010**, *11*, 2674

12:30 Short communication

Photometric characterization of immobilized enzymes on GaN surfaces.

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The biochemical functionalization of AlGaN and GaN surfaces by silanization and subsequent immobilization of biomolecules has recently been demonstrated and the adequacy of AlGaN/GaN field-effect transistors (FETs) for the realization of pH-based enzymatic sensors has been shown [1,2]. The reliability of enzyme-modified FETs sensitively depends on the functionality of the employed enzymes after immobilization on the gate area. In the present work we have applied a photometric method [3] to characterize the activity of penicillinase after covalent immobilization on silanized GaN surfaces. The enzymatic constants have been extracted from recorded absorption transients by advanced modeling using Michaelis Menten kinetics. We have compared the characteristics of covalently immobilized and physisorbed enzymes on GaN to those of free enzymes to assess the impact of the immobilization process. We demonstrate the functionality of covalently immobilized penicillinase over several weeks.

[1] B. Baur, G. Steinhoff, J. Hernando, O. Purrucker, M., Tanaka, B. Nickel, M. Stutzmann, and M. Eickhoff, Appl. Phys. Lett. **87**, (2005) 263901.

[2] B. Baur, J. Howgate, H.-G von Ribbeck, Y. Gawlina, V. Bandalo, G. Steinhoff, M. Stutzmann and M. Eickhoff, Appl. Phys. Lett. **89**, (2006) 183901.

[3] R. P. Novick, Biochem J. (1962) **83**, 236.

12:45 Short communication

Gold Nanoparticles as Support for the Direct Electron Transfer and Catalysis of the Human Sulfite Oxidase

Stefano Frasca[1], Oscar Rojas[1], Johannes Salewski[2], Inez M. Weidinger[2], Silke Leimkuehler[1], Joachim Koetz[1], Ulla Wollenberger[1]

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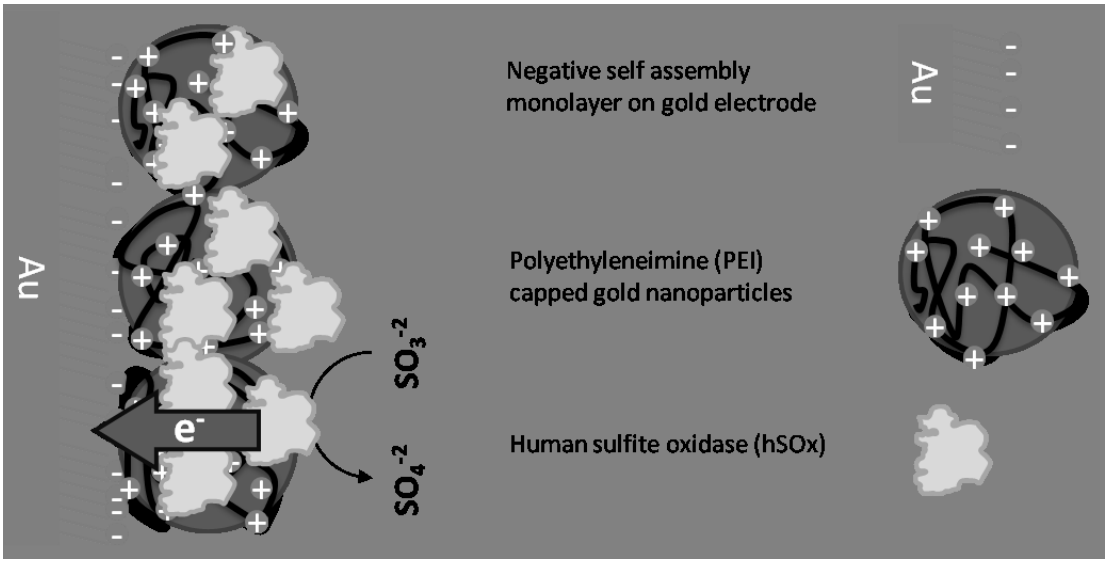
We present the characterization of the direct electron transfer and the catalytic activity of sulfite oxidase in a hybrid biosensor for sulfite detection, consisting of a combination of ultrafine gold nanoparticles and enzyme.
The human sulfite oxidase (hSOx) is a molybdenum and heme containing protein. It catalyzes the oxidation of sulfite to sulphate releasing the electrons to an external acceptor. The natural electron acceptor, cytochrome c, may be used to transfer electrons to an electrode [1] or may be replaced by a chemically modified electrode [2]. On positively charged surfaces the electron transfer proceeds through the heme domain of sulfite oxidase. In order to increase the efficiency of the bioelectrocatalysis we introduced nanoparticles. A hybrid system with an Au-electrode, self assembled alkyl thiol derivatives, polyethylene imine capped nanoparticles and sulfite oxidase has been created. The nanoparticles had a core size of about 6 ± 2 nm nm and a hydrodynamic diameter of 9 ± 1 nm.

Electrochemical as well as UV-vis and SERRS characterization of the system will be presented.



[1] Spricigo R., Dronov R., Rajagopalan K. V., Lisdat F., Leimkühler S., Scheller F. W., Wollenberger U. Soft Matter, 2008, 4, 972.
[2] Sezer M., Spricigo R., Utesch T., Millo D., Leimkühler S., Mroginski M. A., Wollenberger U., Hildebrandt P., Weidinger I. M. Phys Chem Chem Phys., 2010, 12, 7894-7903.

Lunch Break

Saturday afternoon, 5 November, 13:00

Afternoon Session 1

Saturday afternoon, 5 November, 14:00
Chair: Gheber and Boukherroub

14:00 Tutorial lectore

Supramolecular Solar Cells

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Supramolecular chemistry - chemistry of non-covalent bonds includes different type of interactions including ion-pairing, ion-dipole, dipole-dipole, hydrogen bonding, cation-p and Van der Waals forces. Preorganisation and complementarity are the two most important criteria for building efficient host-guest systems that paves ways to mimic the events occurring in nature. Consequently, wide applications based on supramolecular concepts have evolved in recent years. This includes enzyme mimics for catalysis, molecular wires, rectifiers, photochemical sensors and so on. Recently, supramolecular chemistry is also being explored in energy harvesting and storage applications with a dream of building efficient devices for these applications. In this contest, few light energy harvesting devices have been reported based on supramolecular techniques. Here we report building supramolecular light energy harvesting devices using axial ligation and anion binding strategies with the perspective of building efficient system

using custom designed sensitizers. Our approach involves modification of TiO_2 with receptor sites followed by decoration of sensitizers via host-guest self-assembly approach. Due to the nature of the self-assembly methods, the mediating electrolyte solution is made out of a non-coordinating solvent. In such photocells, we were able to achieve high incident-photon-to-current (IPCE) conversion efficiency.

14:40 Keynote lecture

Electrochemical Modelling of Nanoparticle Toxicity

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This talk describes the interaction of SiO_2,ZnO and organic polymeric nanoparticles with the chip-supported phospholipid membranes [1] of the ENNSATOX nanosensor. SiO_2 dispersions of particle size 14 to 150 nm were tested and were found to be stable within the time of the experiment. The interaction of SiO_2 particle dispersions with dioleoyl lecithin (DOPC) membranes were characterised by an interference with the electrically-induced phase transitions (Figure 1) and inversely related to the particle size (Figure 2) and impedance measurements of the SiO_2-DOPC interaction confirmed this finding. Uniquely novel experiments using scanning electron microscopy (SEM) showed that SiO_2 nanoparticles of all size ranges adsorbed on the DOPC surface (Figure 3). It can be concluded from these results that the relationship of SiO_2 activity on the DOPC membrane with particle size is due to the geometrical proximity of the SiO_2 surface to the DOPC polar groups. A one parameter geometric model was fitted to the data as shown in Figure 3 and an interfacial distance of 3.2nm was estimated within which the SiO_2 surface influenced the fluidity of the DOPC.

Similar experiments were carried out with ZnO nanoparticle dispersions from different sources. Only the ZnO dispersions of small particle size were found to interact strongly with the DOPC membrane. The solubility of the ZnO and the release of Zn^{2+} from the nanoparticles was also measured using the ENNSATOX nanosensor. In comparison with the inorganic nanoparticles, experiments were also carried out investigating the interaction organic polymers and organic polymeric nanoparticles with DOPC membranes. The polymers showed considerably stronger DOPC membrane activity. The rates of interaction of the inorganic nanoparticles, the organic polymers and the organic polymeric nanoparticles with the DOPC membrane are compared.

The biological relevance of the ENNSATOX nanosensor has been tested by intercalibrating the results from the sensor with those obtained from the interaction of the nanoparticles with biological organisms of increasing levels of complexity.

References

[1] Z. Coldrick, et al 2009, Electrochim.Acta **54,**4944-4962.

15:00 Short communication

Poly-CPDT films decorated with dinuclear Re(I) complex chromophore pendants: electrochemical and spectroscopic properties

Valentina Bonometti, Patrizia R. Mussini[1], Giuseppe D'Alfonso[2], Monica Panigati[2], Giovanni Rampinini[3], Francesco Sannicolò[3], Elsa Quartapelle Procopio[2]

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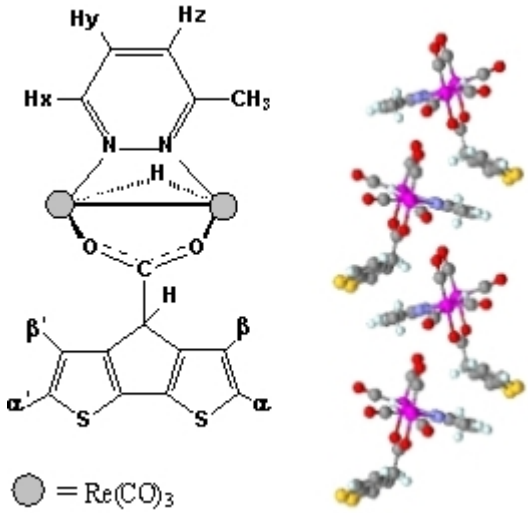

In our current development of new classes of luminescent dinuclear Re(I) complexes, looking for innovative hybrid materials for solid-state devices, we have synthesized and electrochemically characterized the compound Re2(CO)6(μ-H)(μ-3Me-pydz)(μ-OOC- cpdt), a novel conjugate between a luminescent complex and a cyclopentabithiophene (cpdt) unit. By comparison with the corresponding free dinuclear Re complex and with the free HOOCcpdt ligand the CV peaks of the new conjugate have been assigned to the different redox centers. Efficient and very regular electrochemical polymerization has been obtained on GC, Pt, and ITO electrodes as a consequence of the high polymerization ability and regioselectivity of the terminal α-thiophene positions of cpdt. The resulting films have been characterized by CV, EQCM, EIS and UV-vis spectroelectrochemistry. They are stable even upon repeated cycling, exhibiting two subsequent reversible oxidation peaks, whose relative charge ratio is regularly depending on the potential scan rate (possibly, on account of different rates of the counter ion ingress/egress). They also exhibit conspicuous charge trapping features, in terms of both quantity and stability, and excellent electrochromic properties

15:15 Short communication

Surface-modified TiO_2 in optoelectronics

Agnieszka Podborska[1], Konrad Szacilowski[1,2]

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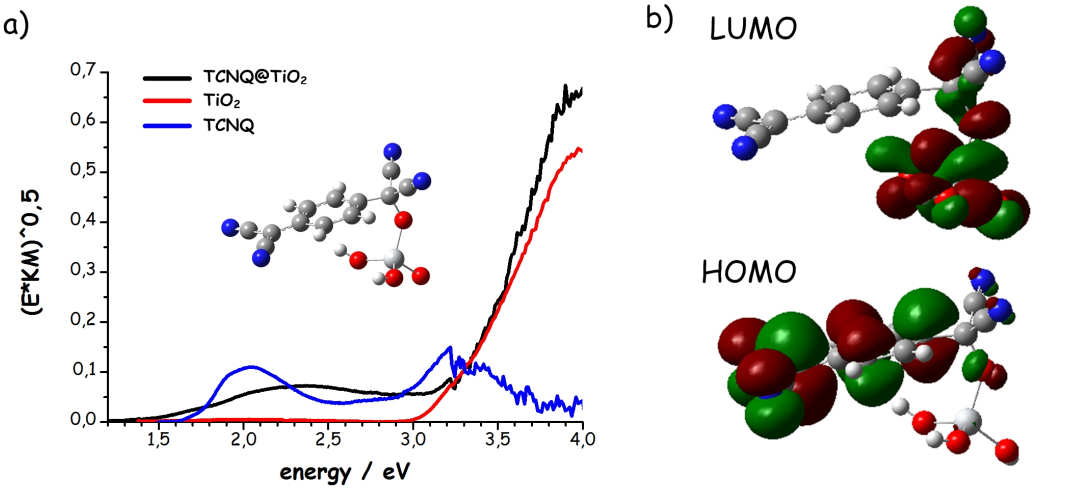
The most popular wide band gap semiconductors, such as TiO_2 or ZnO, have (more or less) suitable electronic properties but their absorption is mostly confined to the ultraviolet region. One of the opportunities to improve optical properties of wide band gap semiconductors is modification of the surface of particles. The most interesting materials, in point of view of optoelectronics, are hybrid materials showed photoelectrochemical photocurrent switching (PEPS) effect. This effect can be defined as switching of photocurrent polarity on change in photoelectrode potential and/or incident light wavelength. This effect was observed in some surface-modified TiO_2 materials [1-4].



Combination of 7,7',8,8'-tetracyanoquinodimethane (TCNQ), which is a good one-electron acceptor, with titanium dioxide (TiO_2) results new hybrid material with unique properties. The photosensitization effect is observed and the absorption range in this material reaches 550 nm. In the diffused reflectance spectra a new absorption peak was observed as a result of surface complex formation (Fig. 1).

Photoelectrodes prepared from this hybrid material exhibit the PEPS effect. Changing the wavelength or the photoelectrode potential easily switches the direction of photocurrent. At positive polarization of the photoelectrode only anodic photocurrent are observed as it can be expected for *n*-type semiconductor. At more negative potentials only cathodic photocurrent are observed.

Photoelectrochemical and spectroscopic studies allowed the elucidation of the mechanism of photocurrent switching. This mechanism is based on photoinduced electron transfer processes from TCNQ molecule to TiO_2 particle. Geometry and electronic structure calculations using DFT method confirmed this mechanism.

Photoelectrochemical properties of TCNQ@TiO_2 materials seem to be suitable for construction of simple logic gates or more advanced logic devices, such as demultiplexer [5-7].

[1] S. Gawęda, G. Stochel, K. Szaciłowski, *Chem. Asian J.***2**, 580-590 (2007)

[2] K. Szaciłowski, W. Macyk, M. Hebda, G. Stochel, *ChemPhysChem*, **7**, 2384-2391 (2006)

[3] K. Szaciłowski, W. Macyk, W. *Chimia*, **61**, 831-834 (2007)

[4] S. Gawęda, G. Stochel, K. Szaciłowski, *J. Phys. Chem. C*, **112**, 19131–19141 (2008)

[5] A. Podborska, K. Szaciłowski*, Austr. J. Chem*. **63**, 165-168 (2010)

[6] J. Mech, R. Kowalik, P. Kwolek, A. Podborska, K. Szaciłowski, *Austr. J. Chem*. **63**, 1330-1333 (2010)

[7] S. Gawęda, R. Kowalik, P. Kwolek, W. Macyk, J. Mech, M. Oszajca, A. Podborska, K. Szaciłowski *Isr. J. Chem.*, **51**, 36–55 (2011)

Coffee break

Saturday afternoon, 5 November, 15:30

Afternoon Session 2

Saturday afternoon, 5 November, 16:00
Chair: D'Souza and Nelson

16:00 Tutorial lectore

Systematic Miniaturization of Microarrays

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The present microarray technology produces active spots with a diameter of ~100 μm and separation of 300 – 400 μm. These sizes are the main reason for the fact that microarray handling requires heavy machines within well equipped laboratories with well trained personnel. To harness the potential of parallel, multiplexed assays and produce portable, deployable, multiplexed sensors, for the monitoring of the environment, a drastic reduction in sizes is required. While nano-biolithography techniques have the ability to fabricate structures of biomolecules as small as ~ 40 nm, very few examples of working biosensors of these sizes have been demonstrated.

We are developing nano-biolithography techniques to produce spots of sub-μm diameters[1-3], while maintaining a high SNR[4], aided with mathematical modeling. We are also tackling additional factors impeding portability of arrayed biosensors, by using polymeric detection elements (molecularly imprinted polymers – MIPs) for stability and regenerative properties[5], detecting binding of analytes using label-free surface-enhanced Raman spectroscopy (SERS)[6-8], and integrating on-chip polymer microlenses-as part of the read-out system[9].

We present results from each of these, discuss the complex inter-dependencies between the various factors, and ways to overcome some difficulties.

References

1. 1. Taha, H., et al., Applied Physics Letters, 2003. **83**(5): p. 1041-1043.
2. 2. Ionescu, R.E., R.S. Marks, and L.A. Gheber, Nano Letters, 2003. **3**(12): p. 1639-1642.
3. 3. Ionescu, R.E., R.S. Marks, and L.A. Gheber, Nano Letters, 2005. **5**(5): p. 821-827.
4. 4. Tsarfati-BarAd, I., et al., Biosensors and Bioelectronics, 2011. **26**(9): p. 3774-3781.

5. 5. Belmont, A.-S., et al., Applied Physics Letters, 2007. **90**(193101): p. 1-3.
6. 6. Kantarovich, K., et al., Analytical Chemistry, 2009. **81**: p. 5686-5690.
7. 7. Kantarovich, K., et al., Applied Physics Letters, 2009. **94**(194103): p. 1-3.
8. 8. Kantarovich, K., et al.,. Biosensors and Bioelectronics, 2010. **26**: p. 809-814.
9. 9. Sokuler, M. and L.A. Gheber, Nano Letters, 2006. **6**(4): p. 848-853.

16:40 Keynote lecture

Droplet based lab-on-chip microfluidic microsystems for high sensitive mass spectrometry analysis

Florian Lapierre, Gaëlle Piret, Guillaume Perry, Vincent Thomy, Yannick Coffinier, Rabah Boukherroub

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Since the emergence of Lab-On-Chip applications for biomedical protocols, electrowetting on dielectric-digital microfluidic (EWOD-DMF) systems have been implemented in many domains such as enzyme assays, immunoassays, DNA-based applications, cell-based assays, tissue engineering and proteomics [1,2]. Thus, Digital MicroFluidic (DMF) Lab-On-Chip devices have been coupled with off-line Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry (MALDI-MS) analysis as an alternative to optical methods [3]. MALDI-MS analysis brings the advantage of time reduction, less complexity of sample preparation and high sensitivity. Even though this system is a pioneering one in the LoC applications for MS analysis, several drawbacks can be underlined: proteins or peptides concentrations remain still quite high (> nmol/µL) and the analysis protocol is somewhat time consuming and complicated due to manipulation of viscous matrix and to proteins drying on the surface.

In this presentation, I will discuss an original study consisting of coupling EWOD-DMF and matrix-free Laser Desorption/Ionization Mass Spectrometry (LDI-MS) analysis using superhydrophobic nanostructured silicon substrates. Compared to a classical hydrophobic surface, it leads to an improvement of the microfluidic actuation (both in terms of minimal applied voltage threshold and droplet speed) and it allows a matrix free LDI-MS analysis of very low concentration of peptides sample (down to fm/µL) through a rapid and simple protocol (without addition of any organic matrix) [3-6].

[1] L. Malic, D. Brassard, T. Veres and M. Tabrizian, *Lab Chip* 10 (2010) 418-431.

[2] V. Srinivasan, V. Pamula, and R. Fair, *Lab Chip* 4 (2004) 310-315.

[3] A. R. Wheeler, H. Moon, C. A. Bird, R. R. O. Loo, C. J. Kim, J. A. Loo, R. L. Garrell, *Anal. Chem.***77** (2005) 534

[4] F. Lapierre, G. Piret, H. Drobecq, O. Melnyk, Y. Coffinier, V. Thomy and R. Boukherroub, *Lab Chip*11 (2011) 1620-1628.

[5] M. Jönsson-Niedziolka, F. Lapierre, Y. Coffinier, S. J. Parry, F. Zoueshtiagh, T. Foat, V. Thomy, R. Boukherroub, *Lab-on-Chip* 11 (**2011**) 490-496

[6] G. Perry, V. Thomy, M. R. Das, Y. Coffinier and R. Boukherroub (**2011**)

17:00 Short communication

Electrochemical Nanofluidic Biosensors

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Phenolic compounds include a large variety of analytes relevant in health care and pollution monitoring. Tyrosinase is an enzyme which has broad substrate specificity toward a broad range of phenols. It converts electrochemically inactive monophenols into active quinones, and most tyrosinase biosensors are based on the electrochemical reduction of quinone produced by the enzymatic reaction. Immobilization of the enzyme while retaining its specific biological function, is a key step in the construction of enzyme-based biosensors because it ensures an intimate contact between the enzyme and the underlying transducer, can improve enzyme stability, and largely determines the ultimate sensor performance.

Here, we present our recent data for measurement of tyrosinase kinetics using electrochemical methods and compare the results with those obtained from UV-Vis spectrophotometry. Further, we show the procedure for immobilization of tyrosinase in a thin layer cell. The immobilization method is based on introducing sulfhydryls group into the enzyme through a bifunctional linker which then can bond to the gold electrode surface via thiol bonds. The electrode is placed in a thin layer cell of volume 3×10^{-10} m^3. Different parameters including immobilization time, incubation time, and phenol concentration are studied. Our study shows that the enzyme remains active after immobilization and that activity can be measured even with small amounts of immobilized enzyme.

17:15 Short communication

Inherently chiral conducting polymer electrodes

Patrizia R. Mussini[1], Francesco Sannicolò[2], Valentina Bonometti[1], Ester Giussani[1], Wlodzimierz Kutner[3], Krzysztof R. Noworyta[3], Tiziana Benincori[4], Simona Rizzo[5], Roberto Cirilli[6], Monica Panigati[7], Sergio Abbate[8], Giovanna Longhi[8], Ettore Castiglioni[9]

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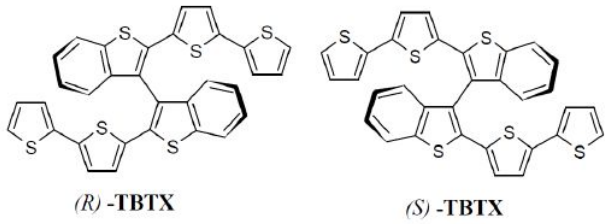
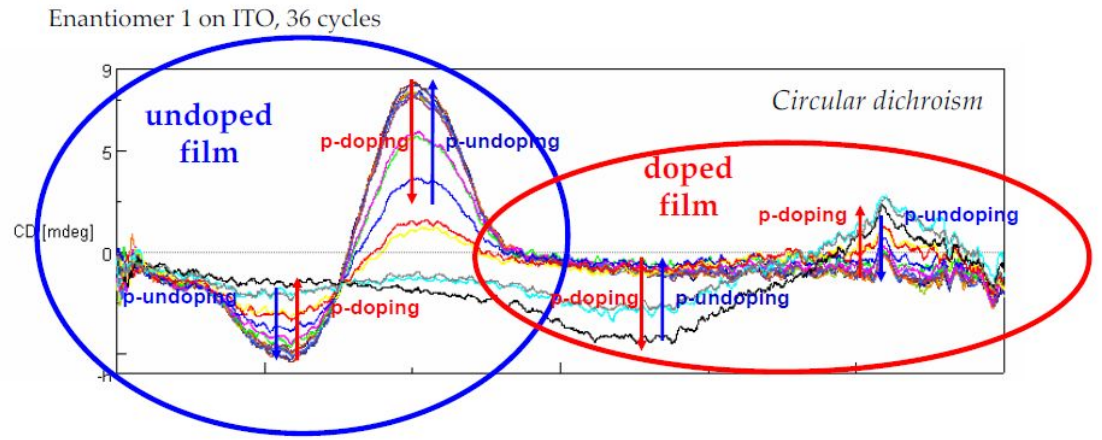
The availability of materials able to couple electroactivity and enantiorecognition capability is an ambitious objective of the current chemical research, aiming to both electrically triggered enantioselective electron transfers and electrically monitored enantioselective recognitions. Ideal candidates are organic conducting polymers, several of which have been functionalized with chiral pendants; this "localized" approach, however, appears to lead to poor chirality manifestations. We present *inherently* chiral conducting films prepared by electropolymerization of monomers like the TBTX molecule in the figure, where chirality is owed to a tailored torsion internally produced along the whole conjugated backbone, and not to the presence of stereocentres external to the conjugated chain. Both enantiomer films have been characterized together with the racemate one by CV, EIS, and circular dichroism with *in-situ* electrochemistry. Positive charge injection, reducing the torsion angle to achieve better π system conjugation, results in a fully reversible "breathing" process of the 3D chiral conducting network upon potential cycling. Enantiorecognition

capability tests on chiral probe molecules are in progress.





17:30 Short communication

Surface modification of gold electrodes for a switchable biosensor

Clement Comminges[1], Martin Sütterlin[2], Erik Wischerhoff[3], Birgit Dietzel[4], Burkhard Schulz[4], Konstanze Stiba[1], Silke Leimkuehler[1], Ulla Wollenberger[1]

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Phase transition polymers swell or collapse in aqueous media as a response to external stimuli. This transition can be triggered by a change in temperature, pH, ionic strength or even by a binding event based on biochemical recognition. The latter makes them attractive candidates for switchable elements of biosensors. The goal of this work is to develop a readout system for biomolecular interactions based on the structural changes within a polymer triggered by a specific binding event and an enzymatic reaction as signal amplification.

For this purpose, two architectures for surface modification are investigated. Both are built in two steps: First, a layer-by-layer (LBL) assembly is prepared on the surface of a gold electrode. In a second step, a terminal layer containing a polymerization initiator is used to grow a LCST (Lower Critical Solution temperature) polymer from

the surface. Enzyme immobilization takes place either in the LBL assembly (fig. 1a) or in the LCST-polymer matrix (fig. 1b). The assembly steps are monitored by Quartz Crystal Microbalance with Dissipation (QCMD). The switching behavior of these modified electrodes is then assessed by measuring the charge transfer resistance and transformation of a redox mediator for the enzymatic reaction as a function of temperature. The catalytic efficiency of the enzyme is determined by (spectro)electrochemical methods.

We report on the synthesis and characterization of these modified surfaces. These preliminary results demonstrate the possibility of immobilizing the enzymes underneath or inside the switchable polymer cover. In further steps, the switchable polymer brush will be furnished with virus recognition sites to implement the biosensing functionality.

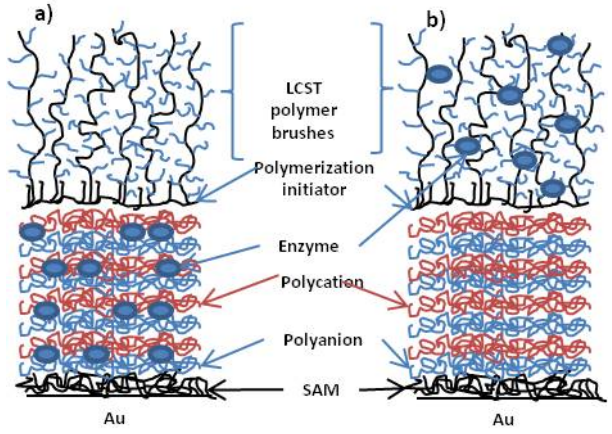

Figure 1: Electrode architecture with enzyme immobilized in the LBL assembly (a) or in the LCST polymer matrix (b).

17:45 Short communication

A role of phosphonium-phosphate ionic liquid in anion-sensing mechanism at toluene-modified electrode

Wojciech Adamiak[1], Galyna Shul[1], Ewa A. Roznicka[1], Masanori Satoh[2], Jingyuan Chen[2], Marcin Opallo[1]

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A continuous interest in liquid modified electrodes is probably due to their unique property which is a well defined liquid-liquid interface. Typically, liquid deposits consist of water immiscible organic solvents in the form of droplet arrays [1], single droplets [2], or thin films [3], and the electrode is immersed in an aqueous electrolyte. In the majority of the studies, this organic liquid contains redox active molecules. The electron exchange between the redox probe and the electrode leads to a charge imbalance within the liquid deposit and the electrode reaction is followed by ion transfer across the liquid-liquid interface. In many cases these liquid modified electrodes exhibit ion-sensitive voltammetry, because ions have different affinities to the adjacent phases as defined by their standard transfer potentials.

In this work an electrochemical behavior of trihexyl(tetradecyl)phosphonium tris(pentafluoroethyl)trifluorophosphate ionic liquid ($P_{14,6,6,6}FAP$) modified electrode has been examined in terms of interfacial ion transfer. Manganese(III) tetraphenylporphyrin chloride ($MnTPP^+Cl^-$) and ionic liquid supported toluene have been utilized as a redox probe and a water immiscible phase, respectively.

Electrochemical studies of ion transfer have been preceded by a single phase study of $MnTPP^+Cl^-$ in toluene-$P_{14,6,6,6}FAP$ mixture in order to evaluate its interactions with this electrolyte. A blue shift of characteristic bands at

UV-Vis spectra of the porphyrin have been observed as the concentration of $P_{14,6,6,6}FAP$ was increased. Voltammetric studies and theoretical calculations of steady state currents revealed a decrease of porphyrin diffusion coefficient in the presence of $P_{14,6,6,6}FAP$. All these facts have been assigned to a significant Cl^- exchange for a large FAP^- anion at the axial position of the porphyrin complex.

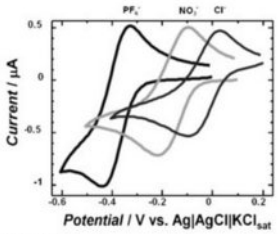

Fig.1. Effect of aqueous anions on cyclic voltammograms obtained at glassy carbon electrode coated with toluene solution containing 1 mM Mn(III)TPP$^+$Cl$^-$ and 0.4 M $P_{14,6,6,6}FAP$. The electrode was immersed into 0.1 M aqueous solutions of KPF_6, KNO_3, and KCl. Scan rate was 10 mV s^{-1}.

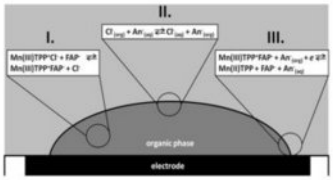

Fig.2. Scheme of the processes that occur at organic liquid modified electrode used in this study. I. interphase reaction of ion exchange between Mn(III)TPP$^+$Cl$^-$ and the ionic liquid anion (FAP^-), II. interfacial anion exchange between organic and aqueous phase, III. coupled electron and ion transfer reaction responsible for anion-sensitive voltammetry.

Under biphasic conditions the electrode surface was modified by a ca. 30 um layer of the organic phase deposited by a solution-cast method. Voltammetric measurements revealed that MnTPP mid-peak potential depends on the nature (Fig.1.) and concentration of the aqueous electrolyte anion. A Nernst type equation has been derived to describe this dependence and anion-sensing mechanism has been evaluated. It has been proposed that heterogeneous electron transfer is followed by anion expulsion where the anion sensitivity results from lability of the axial coordination site of $MnTPP^+Cl^-$ and from spontaneous ion exchange (Fig.2.). This work can possibly contribute to application of toluene-based media in electroassisted ion extraction or in development of novel amperometric sensors.

References:

[1] F. Marken, R. D. Webster, S. D. Bull, S. G. Davies, J. Electroanal. Chem. 1997, 437, 209.

[2] F. Scholz, S. Komorsky-Lovric, M. Lovric, Electrochem. Commun. 2001, 3, 112.

[3] C. Shi, F. C. Anson, Anal. Chem. 1998, 70, 3114.

Dinner

Saturday evening, 5 November, 18:00

Poster Session

Saturday evening, 5 November, 19:00

19:00 Poster 1

Molecularly imprinted polymer (MIP) chemosensors for surface plasmon resonance (SPR) and differerntial pulse voltammetry (DPV) determination of melamine

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Melamine is a small molecule, amine that is illegally used to artificially increase protein reading in dairy products [1]. Long-term exposure to melamine may cause formation of lethal kidney stones in humans [2]. Preparation of

molecularly imprinted polymer (MIP) film sensitive to melamine and its integration with a piezomicrogravimetric sensor by means of electropolymerization has already been reported [3]. In the presented work, the previously synthesised functional and cross-linking monomers were used to prepare a recognition unit for the surface plasmon resonance (SPR) and differential pulse voltammetry (DPV) chemosensors. Parameters of the MIP preparation, like composition of the solution for electropolymerization, the type of solvent used for template extraction, and film thickness, were optimized in order to obtain a recognition film with appreciable both the limit of detection and the dynamic linear concentration range for melamine determination. Thickness of the MIP film was measrued using spectroscopic ellipsometry and atomic force microscopy. The limit of detection reached the range of tens of micromoles and nanomoles, and the linear concentration range attained the level of milimoles and nanomoles for SPR and DPV, respectively.

References

[1] E. L. Bradley, V. Boughtflower, T. L. Smith, D.R. Speck, L. Castle, *Food Addit. Contam.* 2005, 597.

[2] R. L. Dobson, S. Motlagh, M. Quijano, R. T. Cambron, T. R. Baker, A. M. Pullen, B. T. Regg, A. S. Bigalow-Kern, T. Vennard, A. Fix, *Toxicol Sci,* 2008, 251.

[3] A. Pietrzyk, W. Kutner, R. Chitta, M. E. Zandler, F. D'Souza, F. Sannicolo, P. R. Mussini, *Anal. Chem.* 2009, 10061.

19:00 Poster 2

Tuning Electron Transmission Efficiency through Peptides: Modulation by Mechanically Induced Structural Changes

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Self-assembled monolayers of α-helical peptides were prepared on gold and the effects of the monolayer structure on long-range electron transfer through the helical peptides were studied. Electron transport properties of helical peptides were investigated using atomic force microscope with a conducting tip. The helical peptides contained 8, 10, 12 and 14 amino acids residues. A cysteamine linker at the C-terminus and cystamine residue (with Boc protected amino moiety) at the N-terminal were introduced in order to provide covalent contact either with gold substrate or tip. Current-voltage characteristics of these junctions were probed as a function of SAM thickness and the load applied to the microcontact. The electrical behavior and the exponential dependence of current vs peptide chain length are consistent with coherent, nonresonant electron tunneling across the SAM. These measurements show that conducting probe-AFM is a reliable method for fundamental studies of electron transfer through small numbers of molecules. The ability to vary the load on the microcontact is an important feature of these junctions, whichopens opportunity to explore electron transfer efficiency as a function of molecular deformation.

19:00 Poster 3

Designing biosensors based on semiconductor nanoparticles for an early detection of neurodegenerative diseases.

Bożena Sikora[1], Krzysztof Fronc[1], Izabela Kamińska[1], Anna Baranowska-Korczyc[1], Kamil Sobczak[1], Kamil Koper[2,3], Jakub Włodarczyk[4], Piotr Krakowian[5], Tomasz Wojciechowski[1], Grzegorz M. Wilczyński[4], Wojciech Paszkowicz[1], Tomasz A. Kowalewski[5], Piotr Stępień[2,3], Danek Elbaum[1]

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Neurodegenerative diseases are a group of progressive congenital or acquired diseases of the nervous system, in which the primary pathological phenomenon results from cellular dysfunctions. The first behavioral symptoms appear when a significant number of neurons are damaged. The lack of effective drugs is predominantly associated with unavailability of diagnostic tools for an early stage of neurodegenerative disease development.

Our aim is to design a biosensor based on semiconductor nanoparticles ZnO/MgO for an early detection of neurodegenerative diseases. Despite several advantages of nanoparticles (small size, lack of fotobleaching) they have a flaw, due to their relatively low sensitivity to the external environment. Therefore, they require passivation with biologically specific probes. We have covered ZnO/MgO nanoparticles with carboxymethyl-beta-cyclodextrin (CMCD) which serves a role of a linker. The interior of the cyclodextrin is hydrophobic so it can form inclusion complexes with hydrophobic molecules.

We examined FRET between the nanoparticles of ZnO/MgO coated beta-cyclodextrin and organic dye (Nile Red) built into cavities of the cyclodextrin. We studied the effect of temperature on the FRET system. In the first stage, we introduced the FRET complex into HeLa cells. The emission maxima of the FRET nanoparticles inside the cells was 630 nm, while outside the cells was observed to be 610 nm. Thus, we were able to design a prototype of a biosensor sensitive to the local cellular environment. In the next stage, we intend to introduce the FRET complex into neurons.

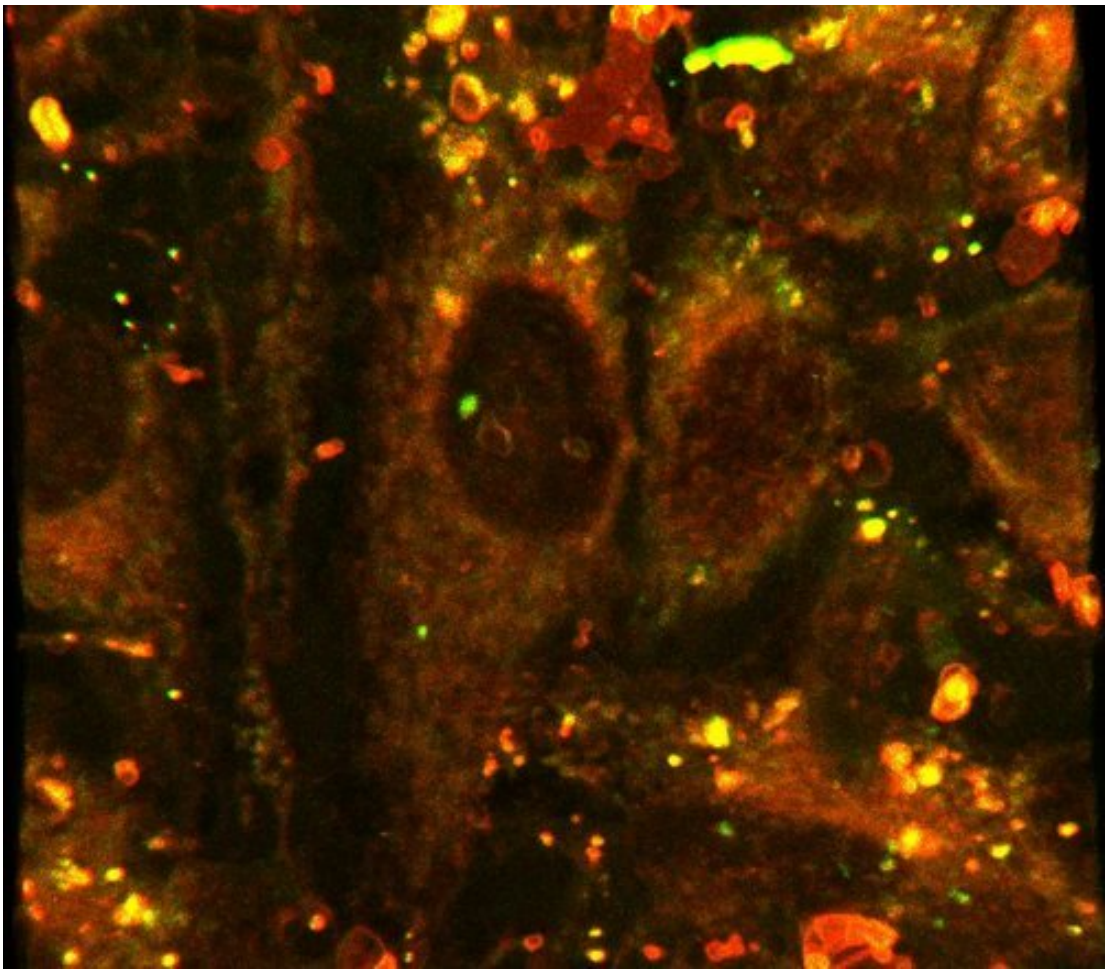

Figure 1. HeLa cells with FRET complex. Green: cells autofluorescence (ex. 488 nm), red: FRET complex (ex. 560 nm).

Acknowledgements: The research was partially supported by the European Union within European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08) and was partially supported by the Ministry of Science and Higher Education (Poland) through Grant No. N N518 424036 **,** andgrant from the Polish National Centre for Research and Development NR13004704.

19:00 Poster 4

Synthesis and properties of $NaYF_4$: Er, Yb, Gd nanoparticles with and without SiO_2 coating for biomedical applications.

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Cell autofluorescence is an important limitation in majority of applications based on luminescent probes. In addition, most biological structures absorb ultraviolet and visible light. On the other hand, significantly lower absorption and resulted autofluorescence of the near infrared energy (wavelength 700 - 1000 nm) is observed for biological materials.

Our aim was to synthesize $NaYF_4$ nanoparticles doped with up-converting rare earth metals(Er, Yb). The conversion takes place by a multiphoton absorption of a low-energy radiation (near infrared – optimum 980 nm) and subsequent emission of higher energy radiation (visible light). Synthesized up-converting nanoparticles were subsequently coated by a layer of SiO_2 for the protection of biological systems from the toxic effects of fluoride and subsequent attachment to biologically active molecules.

We synthesized $NaYF_4$ nanoparticles doped by 2 % Er and various Yb concentrations (10 to 30%). Nanoparticles excited by infrared light (965 nm) have two luminescence bands: the first with a maximum at 540 nm and the second, more intense band, with a maximum at a wavelength of 670 nm. The most efficient luminescence was observed for nanoparticles doped with 2% Er and 30% Yb.

Synthesized by us nanoparticles have a diameter from 35 to 60 nm as determined by a transmission electron microscopy (TEM) and X-ray diffraction. These methods have confirmed the cubic structure of the nanoparticles. Using TEM we were able to confirm the presence of a thin SiO_2 layer on the surface of nanoparticles.

The upconverting SiO_2 coated nanoparticles were transported into HeLa cells and their luminescence was measured by a confocal microscopy (Figure 1). Subsequently, these nanoparticles were linked to biologically active molecules to created a biosensor based on the Fluorescent Resonant Energy Transfer between the nanoparticles (donors) and organic probe sensitive to the external environment (acceptors).

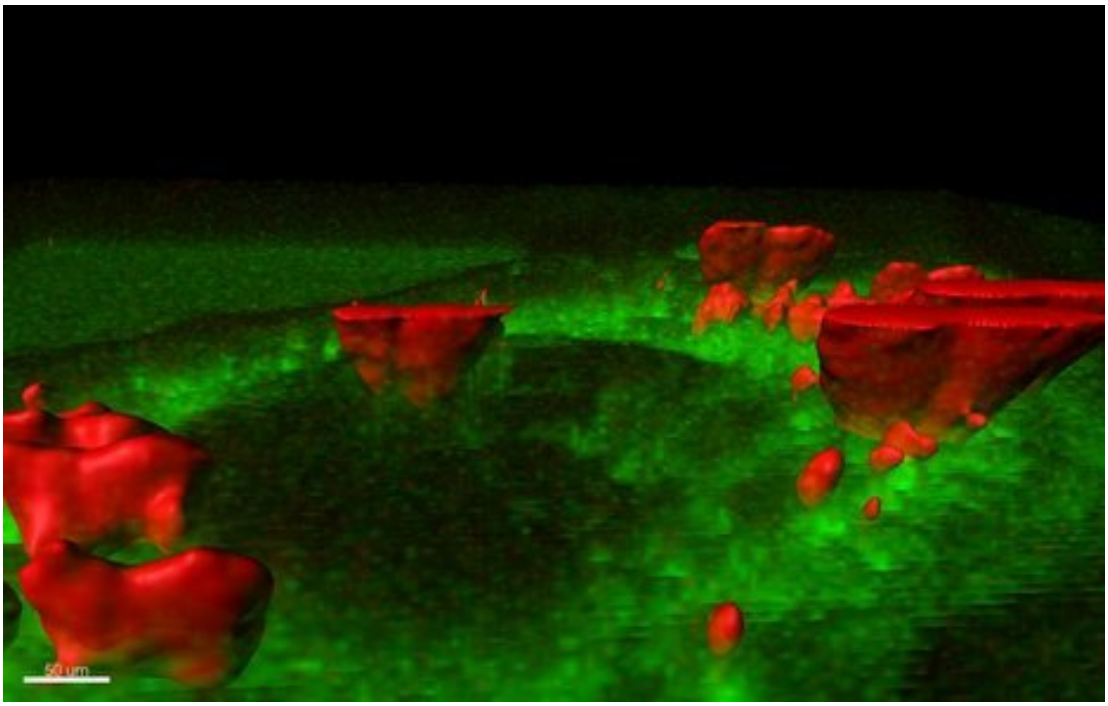

Figure 1. NaYF4: Er, Yb nanoparticles inside HeLa cells. Image obtained from confocal microscopy. Green color: autofluorescence of cells (excitation: 488 nm); red color: NaYF4 nanoparticles (excitation: 960 nm).

Acknowledgements: The research was partially supported by the European Union within European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08) and was partially supported by the Ministry of Science and Higher Education (Poland) through Grant No. N N518 424036**,** and grant from the Polish National Centre for Research and Development NR13004704.

19:00 Poster 5

Electrochemical behaviour of Cytochrome c immobilised in a poly-scopoletin layer

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We investigated the oriented fixation of Cyt c by combining electrostatic binding to a negatively charged SAM with the entrapment by an electropolymer layer in order to increase the stability of the sensor. Three different architectures have been investigated and the electrochemical measurements are given in fig. 1.

(i) Electrostatic adsorption of Cyt c at mercaptoundecanoic acid (MUA) modified gold electrodes:

The values of surface concentration Γ, rate constant k_s and formal potential E^o were chosen according to the literature [1] and reflect a quasi-reversible electron exchange of a monolayer.

(ii) Coverage of the SAM with a poly-scopoletin layer:

The electropolymerization takes place at the MUA coated gold electrode at potentials between 0 V and 1 V versus Ag/AgCl in presence of the water-soluble scopoletin (7-hydroxy-6-methoxycoumarin). The polymer growth is self-

limited by the isolating character of the polymer film. Furthermore, the polymer film is thin, highly hydrophilic and non-conducting. Incubation of the MUA-poly-scopoletin covered gold electrode in a Cyt c containing solution leads to electroactive surface concentrations below a complete monolayer. The values for k_s and the peak separation indicate that the Cyt c is converted at the MUA layer.

(iii) Enhancement of Cyt c adsorption by SDS:

The electrostatic binding of Cyt c to the poly-Scopoletin modified Au-Electrodes (with Q = 0.37 ± 0.02 mC) was enhanced by loading the weakly positive charged polymer layer with negatively charged Sodium Dodecyl Sulfate (SDS). Characterization of this Cyt c coated electrodes showed a formal potential of (-13.48 ± 11) mV vs. Ag/AgCl with a peak separation of 36 mV and a heterogeneous electron transfer constant of 9.75 ± 2 s^{-1}.

The value of the formal potential is in agreement with that for native Cyt c, whilst denaturation would shift the potential into cathodic direction [2]. The electroactive surface concentration of Cyt c is (6.73 ± 2.96) pmol cm^{-2} which is almost 2 times higher than the value of electroactive protein on MUA modified electrodes. These values suggest the participation of more than one layer of Cyt c in the electrode process.

Conclusions

Coverage of the MUA-modified gold electrode by electropolymerized scopoletin leads to an effective architecture for the direct electron transfer of Cyt c. This system will be applied for surface imprinting and sensor development.

References

[1] B. Ge, F. Lisdat "Superoxide sensor based on cytochrome c immobilized on mixed-thiol SAM with a new calibration method" Analytica Chimica Acta 454 (2002) 53-64

[2] A. V. Krylov, W. Pfeil, F. Lisdat "Denaturation and renaturation of cytochrome c immobilized on gold electrodes in DMSO-containing buffers" Journal of Electroanalytical Chemistry 569 (2004) 225-231

The authors gratefully acknowledge the financial support of BMBF (0311993) Germany. This work is a part of UniCat, the Cluster of Excellence in the field of catalysis coordinated by TU Berlin and financially supported by Deutsche Forschunsgemeinschaft (DFG) within the framework of the German Excellence Initiative (EXC 314).

19:00 Poster 6

Mass transfer in Nanofluidic Devices embedded in a Microfluidic Channel

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Electrochemical nanofluidic devices have been introduced at 2008 []. These tiny devices feature two planar microelectrodes (~ 5-10 μm) separated by a thin layer of fluid (with a desired thickness, less than 300 nm) was fabricated on a chip. The fabrication of these channels involves photolithographic patterning in a way that the nanofluidic device is encapsulated in silicon dioxide with two access holes. Access holes are created to reach the metal and etching solution is introduced to remove the metal, leaving behind a nanoscale cavity. Redox active molecules can freely diffuse in and out of the channel and undergo electrochemical redox cycling at both suitably biased potentials. Since these molecules are capable of repetitively undergoing oxidation and reduction, each molecule can transfer, on average, thousands of electrons by repeatedly traveling between the electrodes before escaping back out into the bulk. This leads to a corresponding boost in sensitivity and selectivity. This design offer experimentalists many potential applications in designing new sensors with the option of integration on a chip. The substantial current amplifications provide researchers the opportunity to access lower detection limits. The devices are so far operated under conditions of diffusion controlled mass transport.

Here, we examine the electrochemical response of a nanofluidic device placed inside a rectangular microfluidic cell. Solution was pumped to the cell under laminar flow conditions. In this arrangement, we expect that the material is brought to the device via both diffusion and convection in a microchannel. However, we show that the mass transfer

inside nanofluidic device is not affected by the rate of flow in the microchannel. We validate our experimental data with those obtained theoretically with COMSOL multiphysics.

[1] B. Wolfrum, M. A. G. Zevenbergen and S. G. Lemay, Analytical Chemistry 80, 972 – 977 (2008).

19:00 Poster 7

Biofuel cell based on carbon nanotubes with covalently bonded laccase and glucose dehydrogenase embedded in cubic phase

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Biofuel cell is an electrochemical device that converts chemical energy into electrical using enzymes as catalysts and simple, natural substances e.g. glucose as fuel. [1,2,3] Here, the glassy carbon (GC) and graphite electrodes were modified with laccase from Cerrena unicolor bonded to single-walled carbon nanotubes (SWCNTs) via various linking groups or cross-linked with bovine serum albumin (BSA) by glutaric aldehyde. Anode was composed of glassy carbon electrode, modified with SWCNTs and liquid crystalline cubic phase, containing glucose dehydrogenase. The anode described and GC electrode, decorated with SWCNTs with covalently bound laccase as cathode were successfully used to construct the biofuel cell. The parameters of the cell were evaluated.

References:

[1] A. Zebda, Ch. Gondran, A. Le Goff, M. Holzinger, P. Cinquin, S. Cosnier, *Nature Commun.* in press

[2] T. Miyake, S. Yoshino, T. Yamada, K. Hata, M. Nishizawa, *J. Am. Chem. Soc.* 133 (2011) 5129 - 5134

[3] E. Nazaruk, M. Karaskiewicz, K. Zelechowska, J. Biernat, J. Rogalski, R. Bilewicz, *Chem. Commun* in press.

19:00 Poster 8

Detection of supercoiled and linear plasmid DNA

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Even with highly sensitive voltammetric or potentiometric techniques [1, 2], the detection of weak plasmid DNA signals is problematic. Moreover, plasmid DNA electrochemistry has been mainly studied using reduction signals of the nucleic acid bases on mercury electrodes [1], and rarely the oxidation signals on carbon electrodes [2]. In our initial studies [3-5], we have used methylene blue (MB) entrapment into the superhelical form of pUC19 plasmid [3, 4], and/or deposition of palladium [5] to enhance the oxidation of the pUC19 plasmid. The plasmid layer was adsorbed on glassy carbon electrode, achieving an almost ten fold increase of the DNA signals.

In this work, we have focused on the detection of the oxidation signals of two types of plasmid DNA – pUC19 and pGEX-4T-2 in two forms – superhelical and linear. The oxidation of these two plasmids in two different forms can

be distinguished by their slow adsorption on glassy carbon (GC) electrode from 0.25 M acetic buffer pH 4.7 containing 18 mM $MgCl_2$ and low concentrations (pg/mL) of the plasmids. The adsorption of the plasmids was monitored using SW, DP and AC voltammetry. Smaller (2686 bp) supercoiled pUC19 accumulated faster than larger (4970 bp) supercoiled pGEX-4T-2. Even though both forms of plasmid consisted of the same number of base pairs, we have noticed significant differences between the accumulation of supercoiled and linear forms of these plasmids. Only one broad signal of the oxidation of nucleic acid bases was detected for the linear plasmid, instead of typically observed two signals corresponding to guanine and adenine oxidation.

In the presence of methylene blue, a typical intercalator [6], the oxidation signals of bases are significantly enhanced [3-5], allowing for the detection of the plasmids at concentrations lower than pg/mL. Except for a typical MB signal at -0.2 V vs. SCE, MB(I), another MB oxidation signal at ca. 0.95 V, MB(II), is used to distinguish not only between two different plasmids, but also between their supercoiled and linear forms. The MB(I) signal, typically used to probe DNA intercalation [6], is low or even hardly visible at MB concentrations below 1-2 μM, while in the same MB concentration range, the MB(II) signal increases significantly. The AC voltammetric experiments sensitive to plasmid DNA adsorption in a wide potential range from -0.6 v to 1.4 V suggest that the interactions of MB are related to the capacity and resistance changes of the plasmid layer.

References:

[1] E. Paleĉek; Talanta, 2002, 56, 809

[2] J. Wang, G. Rivas, X. Cai, H. Shiraishi, P.A.M. Farias, N. Dontha, D. Luo; Anal. Chim. Acta, 1996, 332, 139

[3] A. Palinska, H. Elzanowska, A. Ogorek, E. Zwierkowska, S. Achmatowicz, M. Maj-Zurawska; Surface modification for chemical and biochemical sensing, SMCBS'2009, the 4th International Workshop, 6 to 10 November 2009, Przegorzaly near Cracow, Poland

[4] A. Palinska, A. Grodzka, H. Elzanowska, B. Kepska, E. Zwierkowska, S. Achmatowicz, M. Maj-Zurawska; Electroanalysis 2010, 22, 1306

[5] H. Elzanowska, A. Ogorek, P. Kulesza, 61st Annual Meeting of the International Society of Electrochemistry, September 26th, October 1, 2010, Niece, France

[6] Gorodetsky, J.K. Barton, 2006, 22, 7917

19:00 Poster 9

Electrochemically Assisted Sol-Gel Bioencapsulation on Carbon Nanotubes Network

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It is possible to induce the formation of sol-gel layers on electrode surfaces by means of electrochemistry. The concept is based on local pH change near the electrode surface which catalyses the sol condensation and significantly increases the rate of silica deposition only onto the solid surface without disturbing the rest of the sol [1].
Recently it has been shown that this procedure could be applied to the encapsulation of biomolecules in thin silica films while retaining their biocatalytic properties [2]. An interesting perspective of this work concerns the deposition of such composite material on electrodes exhibiting large electroactive surface areas, which would contribute to significantly improve the bioelectrochemical reaction [3].
Carbon nanotubes are important materials for the electrochemical detection of NADH [4]. This molecule is used as a co-factor by a large number of dehydrogenase that can find application in biosensors or enzymatic electrosyntheses. In this context we have evaluated the interest of carbon nanotubes networks obtained by electrophoretic deposition for the oxidation of NADH and the immobilization of dehydrogenases. D-sorbitol dehydrogenase was used as

model enzyme. Immobilization of the biomolecule was achieved by physical entrapment into sol-gel films prepared by the electrochemically assisted deposition.
The carbon nanotubes network catalyses effectively the detection of NADH, this reaction occurs at lower potential than on the glassy carbon substrate. Moreover, the intensity of the oxidation peak depends on the quantity and texture of deposited nanotubes. D-sorbitol dehydrogenase can be immobilized in this network of carbon nanotubes by electrochemically assisted generation of sol-gel layers and the response of the electrode to D-sorbitol is strongly dependent on the electrogeneration time.
[1] R. Shacham, D. Avnir, D. Mandler, *Adv. Mater.***1999**, *11*, 384.
[2] O. Nadzhafova, M. Etienne, A. Walcarius, *Electrochem. Commun.***2007**, *9*, 1189.
[3] Z. Wang, M. Etienne, G.-W. Kohring, Y. Bon-Saint-Côme, A. Kuhn, A. Walcarius, *Electrochim. Acta*, in press.
[4] M. Wooten, W. Gorski, *Anal. Chem.***2010**, *82*, 1299.

19:00 Poster 10

Nanofilter modifiers for cationic and anionic surfactant membrane sensor

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Surfactants are the main raw material in manufacturing cosmetic and hygienic preparations, detergents, cleaners, drugs, food samples, etc. Synthetic surfactants are the mixtures of their isomers, homologues and oligomers. Therefore the quantitative identification and separate determination of them in complex liquids is a difficult analytical problem.

To separately determination of homologous sodium alkyl sulphates $C_nH_{2n+1}OSO_3Na$ (n=10-16) and alkyl pyridinium chlorides $[C_nH_{2n+1}C_5H_5N]Cl$ (n=10-18), for studying physical and chemical membrane characteristics were synthesized the nanofilter membranes with a controlled pore sizes. Different anionic and cationic surfactants were used as pore generators. For design of potentiometric membrane electrodes an ionic associates of alkyl pyridinium and tetraalkylammonium with dodecylsulphate, cetylpyridinium with alkyl sulphates and tetraphenylborate (C_{EAC} = 0,002-0,001 mol/kg of plasticizer) were used as electrode-active components (EAC) of sensor membranes.

A surface of poly(vinyl chloride) plasticized membranes were modified by nanofilter membranes (modifiers) with different pore generators. The main electrochemical characteristics of cationic and anionic surfactant sensors with different membrane composition and sieve pore generators were determined.

Nanofilter membranes let pass those surfactants whose molecules are smaller or comparable in size with the pore generator; bigger ions are retained and do not exhibit their electrode functions. The separability of nanofilter membranes was examined in binary and ternary model mixtures of homologues of separate surfactant types with component ratios. The modified sensors were separately found to determination of individual homologues of cationic and anionic surfactants in mixtures. The pore sizes of our nanofiltering membranes were evaluated by means of electronic microscopy.

The separating power of nanofilter membranes was examined at study of the transport processes (diffusion mass transfer) in a two-compartment cell (sufactant solution with a certain concentration against distilled water) with different nanofiltering membranes between.

The modifying of sensor membrane surfactant surface by nanofilter membranes is promising technique for increase of selectivity of surfactant sensors and separate determination of homologous cationic and anionic surfactants in mixtures.

19:00 Poster 11

Algae Spirogyra sp. – biosensor of surface waters pollution with mercury

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In laboratory the parameters of mercury ions sorption from solutions of $HgCl_2$ by the algae *Spirogyra* sp were investigated. Due to instability of the prepared mercury solutions of concentrations at 0.07 μg Hg/dm^3 level, the preparation procedure was developed which enabled control of changes in mercury concentrations in solution during the sorption process within ± 8%.

To describe equilibrium states the Langmuir isotherm model was used. It was found that algae absorbs mercury proportionally to its content in the solution, with which algae have been in contact.

In next steps several experiments to assess the compatibility of isotherm parameters with the parameters of equilibrium occurring in natural surface waters were performed. In this experiment the processed, lyophilised algae immersed for 30 min. in the studied waters were used. The concentrations of mercury in algae after the process of sorption and in water samples were determined and compared with each other. The determination of mercury in water samples was performed in accordance with EN 1483:2007.

It was shown that algae *Spirogyra* sp. can be used for the biosensor of mercury pollution in surface water.

Mercury concentrations were determined using mercury analyzer AMA 254.

19:00 Poster 12

Titanium dioxide nanotube and enzyme-enhanced photo-bio-fuel cell

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There is an ongoing need to obtain a source of renewable energy harvested, for example, directly from the Sun (1) or a source of energy that is easily accessible and transportable such as oxygen and methanol or oxygen and glucose.

Enzyme modified electrodes have attracted much attention due to their application as catalytic electrodes in bio-fuel cells. (2) Recently we investigated single-walled carbon nanotubes functionalised with 1-pyrenesulfonic acid (PSA) as a means for improving the direct electron transfer to the enzyme bilirubin oxidase. (3) The nanotubes were co-immobilised with bilirubin oxidase in a silicate matrix on tin-doped indium oxide. These electrodes can be used for the bioelectrocatalytic reduction of dioxygen to water from solution.

TiO_2 nanotubes have developed great interest due to their ability to form electrodes with increased effective surface area. In addition, our previous work has shown that the order and smoothness of these vertically aligned TiO_2 nanotubes can be increased resulting in an increase in the electron diffusion length along the tubes and a corresponding increase in conductivity and light to electricity conversion efficiency. (4) Nanostructured semiconducting photo-anodes have been shown by Moore et al. to work in combination with enzyme catalysed oxidation of biofuels. (5) In their work visible light incident on these modified electrodes was shown to result in the photo excitation of a porphyrin dye and the separation of charge. The dye was quenched by β-nicotinamide adenine dinucleotide (NADH) present in the electrolyte solution transforming it ultimately to NAD+. The catalytic oxidation of glucose within the cell in the presence of glucose dehydrogenase (GDH) replenished the supplies of NADH from the oxidised form of this mediator, NAD+, allowing the photo-anode reactions to continue as long as glucose was present.(6)

In this poster we combine two processes – the oxidation reactions driven by a TiO2-modified photo-anode and di-oxygen reduction by enzyme at a CNT-modified cathode – allowing for the formation of novel photo-electrochemical bio-fuel cells. The resulting cells produce a potential difference and a flow of current between the terminals dependent on the intensity of the incident light. Several variations of the cell were constructed so as to investigate the reactions occurring in the cell and so as to determine the dependence of cell performance on cell structure, electrode type and dye type. In addition comparison is made between our results and the existing technology and work published by other groups.

References:

(1) B. O'Regan, M. Grätzel, Nature 1991, 353 (6346), 737

(2) I. Willner, Science 2002, 298, 2407

(3) M. Jönsson-Niedziolka, A. Kaminska, M. Opallo, Electrochimica Acta 2010, 55, 8744

(4) R.P. Lynch, A. Ghicov and P. Schmuki, J. Electrochem. Soc. 2010, 157 (3), G76

(5) A. Brune et al., Langmuir 2004, 20, 8366

(6) M. Hambourger et al., Photochem. Photobiol. Sci., 2007, 6, 431

19:00 Poster 13

Electrochemically Assisted Encapsulation of Bacteria in Sol-Gel Thin Films

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Life-span viability accompanied with preserved activity of micro-organisms in solid support has gained considerable interests for bioelectrochemical applications including biofuel cells and biosensors for environmental monitoring. Sol-gel technology has proved its suitable environment for living cells entrapment and ensured their stability and activity enhancement better than free living cells [1]. The development of the electrochemically assisted deposition of sol-gel at the end of the nineties [2] has opened a larger window for bioencapsulation process in thin sol-gel films by using the electrochemical methods [3]. The Electrochemically assisted deposition has several advantages compared to other sol-gel methods that are based on solvent evaporation (spin-, dip-, spray-coatings). It exhibits the ability of film deposition on small electrodes (ultramicroelectrode) or non-flat supports, in-addition to the film deposition on conducting supports for useful electrochemical applications and monitoring. Moreover, the possibility of porosity control by using the template approach [4] and thickness control facilitates the interactions of trapped living cells with the surrounding environment for fluorescent and environmental analysis.

This communication intends to show some recent developments on sol-gel bioencapsulation using electrochemically assisted deposition applied to the immobilization of bacteria. The incorporation of biocompatible organic polymers to the inorganic sol-gel source has proved the mechanical enhancement of sol-gel deposition and stability. Furthermore, additional disaccharide has provided a more hydrophilic environment which is critical for bioencapsulation of micro-organisms in thin sol-gel film. This hybrid composition of sol-gel appeared to be critical for the long-term viability of trapped bacteria according to the bacterial membrane integrity studied by Live/Dead BacLight viability assay. It proved a better long-term stability of the bacterial membrane integrity than that of inorganic composition of sol-gel [5]. Perspectives of bacterial respiration analysis and bioencapsulation of other complex biological objects with the electrochemically assisted methodology will be discussed later on.

[1] D. Avnir, T. Coradin, O. Lev, J. Livage, *J. Mater. Chem.*, **2006**, *16*, 1013.
[2] R. Shacham, D. Avnir, D. Mandler, *Adv. Mater.*, **1999**, *11*, 384.
[3] O. Nadzhafova, M. Etienne, A. Walcarius, *Electrochem. Commun.*, **2007**, *9* , 1189.
[4] A. Walcarius, E. Sibotier, M. Etienne, J. Ghanbaja, *Nature Mater.***2007**, *6*, 602.

[5] T. M. Harrell, B. Hosticka, M . E. Power, L. Cemke, R. Hull, P. M. Norris, *J. Sol-Gel Sci. Technol.***2004**, *31*, 349.

19:00 Poster 14

Deglycosylation of glucose oxidase by PNGase F

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Many redox enzymes are covered with an insulating carbohydrate core and have their active centers deeply buried inside of the protein structure. Several studies on glycon depletion showed that the carbohydrate shell hinders the electron communication between the active center and the electrode surface. Therefore, accessibility of the prosthetic group can be achieved by removal of the carbohydrate shell, thus giving a possibility to develop mediator-less biosensors.

Present methods for production of deglycosylated enzymes are based on either in-solution digestion of native enzymes, or on production of recombinant enzymes, which lack the carbohydrate shell. However, these methods are time-consuming and expensive. More efficient and cheap way to produce deglycosylated enzymes is desirable.

In attempt to develop a technique for continuous, fast and inexpensive production of deglycosylated enzymes, we have prepared immobilised enzyme reactors (IMERs) with immobilised PNGase F. PNGase F belongs to the class of endoglycosidases, which cleave glycons from Asp residues in N-linked proteins. It was covalently attached to the surface of controlled pore glass (CPG) beads and packed into the IMER. PNGase F was used to deglycosylate glucose oxidase (GOx) containing 6 GlcNAc residues and 3 Man residues. Two IMERs containing 1500 U and 15000 U of the immobilised enzyme were prepared. The efficiency of the two IMERs at different temperatures, as well as time required for complete deglycosylation of GOx, was studied. The degree of deglycosylation was monitored using SDS-PAGE with silver staining. The deglycosylation of GOx was performed both in stop-flow and flow formats with continuous supply of the GOx.

Partial deglycosylation of GOx, subjected to a PNGaseF treatment, resulted in a sharper band on the gel for the native enzyme compared to the non-treated GOx. In a flow experiments band broadening was reduced with decrease of the flow rate from 0.5 mL/min to 0.05 mL/min. For complete deglycosylated enzyme no band for the native GOx was observed.

Complete deglycosylation of GOx was twices faster (1 hour) when using higher amount of PNGase F for preparation of the IMER in a stop-flow experiment. For the same incubation time and the same concentration of GOx, the degree of deglycosylation was higher when performing the reaction at higher temperature (37 °C).

No band for the deglycosylated form of GOx was observed on the gel in any experiments. This is probably due to change in solubility of the deglycosylated form of the enzyme compared to the native form. Since complete removal of the carbohydrate shell from the enzyme results in increased hydrophobicity, it was suggested that the deglycosylated enzyme precipitates on the surface of CPG beads inside the IMER. Addition of up to 20% of organic solvent (methanol) and non-ionic detergent (1% of Triton X-100) did not improve solubility of the deglycosylated GOx.

The advantage of the proposed IMER is that it utilises immobilised enzyme, thus the robustness of the system is greatly improved in terms of operational stability and chemical resistance. The IMER can be reused several times without loss of activity of the immobilised PNGase F, which open an interesting possibility for broad production of deglycosylated enzymes. Therefore, further studies are aiming at fabricating an IMER containing exoglycosidases, which will only perform partial deglycosylation of GOx and other redox enzymes, leaving its solubility properties unaffected.

19:00 Poster 15

Electrochemical communication between viable bacterial cells and flexible redox polymers

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Recently we have shown that bacterial cells can be electrochemically ”wired” to electrodes with flexible redox polymers e.g., poly(1-vinylimidazole)$_{12}$-[Os(4,4’-dimethyl-2,2’-dipyridyl)$_2$Cl$_2$]$^{2+/3+}$ and poly(vinylpyridine) [Os(N,N’-dimethyl-2,2’-biimidazole)$_3$]$^{2+/3+}$. Our initial studies[1] were made with the simple Gram-negative *Gluconobacter oxydans*, where we addressed redox enzymes from the cytoplasmic membrane yielding response for glucose, fructose, ethanol and glycerol. Later focus was on more complex Gram-negative *Pseudomonas putida* and *P. fluorescens*,[2,3] where response currents were obtained for substrates metabolised in the cytoplasmic membrane (glucose) and in the cytosol (phenol). Recently introduction of a cytochrome to the cytoplasmic membrane of *E. coli* facilitated the communication between *E. coli* cells and the redox polymers.[4] In Gram-positive *B. subtili*[5] strain which overproduces complex II, current resonse has been improved several times although it was expected to be more difficult for the thick cell wall to permeate by rodox polymer. Another recent work that supports such a theory is a paper by Marshall and May[6], who show that Gram-positive *Thermincola ferriacetica* strain Z-0001 readily can grow onto a graphite electrode and exhibit direct e^- transfer communication. Currently we are investigating *Rhodobacter capsulatus,* one of the most metabolic versatile bacteria in the nature, grown heterotrophically and successfully wired with poly (1-vinylimidazole) $_{12}$-[Os(4,4’-dimethyl-2,2’bipyridyl)$_2$Cl]$^{2+/+}$, E°’= 200 mV vs. SCE[7] in both batch and flow mode. More experiments are going on to establish the communication between phtoheterotrophicaly grown cells and the redox osmium polymers followed by electrode by using light as a energy source instead of any organic substrate.

References:

[1] I. Vostiar, *et al.*, *Electrochem. Commun.***6** (2004) 621-626.

[2] S. Timur, *et al.,Bioelectrochemistry***71** (2007) 38-45.

[3] S. Timur, *et al.*, *Electrochem. Commun.***9** (2007) 1810-1815.

[4] S. Alferov, *et al.Electrochim. Acta***54** (2009) 4979-4984.

[5] V. Coman, *et al*, *J. Am. Chem. Soc.,***131** (2009) 16171-16176.

[6] C. W. Marshall, H. D. May, *Energy Environ. Sci.***2** (2009) 699-705.

[7] M. N. Zafar *et al.,*Bioelectrochemistry 80(2001)38-42

19:00 Poster 16

Coupling of pyrroloquinoline quinone dependent glucose dehydrogenase (PQQ-GDH) with CytC/DNA multilayer electrodes

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The redox protein cytochrome c (CytC) assembles into electroactive multilayers on gold electrodes. For this purpose desoxyribonucleic acid (DNA) can be utilized as a negatively charged building block. This system can act as a basic construct for the establishment of analytical signal chains when redox enzymes are coupled to these layered assemblies.

One redox enzyme with particular promise is PQQ-GDH, which has an isoelectric point similar to CytC and thus should embed easily. The reaction between CytC and PQQ-GDH has been well investigated when both molecules are in solution: spectrophotometrical- and cyclovoltammetric (CV) analysis show, that PQQ-GDH is able to reduce CytC efficiently. But the reaction between these molecules when both are immobilized on electrodes is a real challenge.

Here we study the electron transfer reaction between PQQ-GDH and CytC with different arrangements. Thus we first assemble a monolayer of CytC on a thiol-modified gold wire electrode. We then place the electrode in a solution of PQQ-GDH. CV-measurements show that a catalytic current occurs in the presence of the substrate (glucose). Next, we investigate the situation when both molecules are immobilized. We use the layer-by-layer deposition technique to assemble a multilayer electrode of CytC, with a terminal layer of PQQ-GDH: (CytC/DNA)n/PQQ-GDH. We find, that a catalytic current flows when glucose is present, proving that inter-protein communication occurs with both surface-fixed components.

This bi-protein multilayer system is sensitive to glucose and the response can be tuned in a certain range by increasing the number of protein layers deposited on the electrode.

19:00 Poster 17

Hybrid electronic tongue for the quality analysis of apple extracts

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Analysis of food products has a particular place in analytical chemistry. Within the food there are still new substances discovered that have a significant impact on human health (for example melamine, NO_2^- ions, mycotoxins, pesticides). For this reason, it is very important to determine the quality of food products. The research is also carried out to assess food origin, specific properties such as nutritional value, and possible contamination.

To ensure adequate monitoring, a lot of the analytical procedures detecting non-compliance with the prescribed standards, are applicable. New solutions that enable rapid and reliable assessment of the quality of the food are of great interest. One of such devices is so-called electronic tongue (ET), which allows to analyze, distinguish and classify liquid samples. ET consisting of sensor arrays and image recognition unit allows for multi-dimensional analysis of chemical images of the samples.

The paper presents the hybrid electronic tongue used in the analysis of extracts obtained from dried apples. The system based on potentiometric and voltammetric sensors, enriched by the data obtained with the use of amperommetry, spectrophotommetry, and conductommetry, allowed for the differentiation of extracts due to the applied food processing (drying technique).

Acknowledgment

This work has been supported by National Center for Research and Development within a framework of LIDER programme (Nr LIDER/17/202/L-1/09/NCBiR/2010), by the European Union in the framework of European Social Fund (through the Warsaw University of Technology Development Programme), and by Project MNS-DIAG Nr POIG.01.03.01-00-014/08-00.

19:00 Poster 18

Nanostructured gold surfaces for biosensing applications

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Gold nanoparticles (AuNPs) have been extensively employed in the development of interfacial platforms for biosensors, since they can be conjugated with biomolecules without interfering with their biochemical activity [1,2]. Particularly, in electrochemical biosensors AuNPs have been used to improve the electron transfer rate and the current response of target electroactive centres/analytes due to their large surface area, high surface free energy and biocompatibility [3].

One of the most important steps in the construction of biosensors is the immobilization of the biomolecule on the substrate and recently, we have demonstrated [4] that a simple one-step method in the presence of CS_2 could be successfully employed in the direct immobilisation of Glucose Oxidase (GOx), from aqueous medium, with the preservation of its bioactivity.

The purpose of this work is to biofunctionalise AuNPs through the one-step reaction between AuNPs, CS_2 and amine groups present in aminoacids (e.g. tryptophan) and enzymes (e.g. glucose oxidase), followed their immobilization onto flat gold electrodes, in order to improve the electrochemically transduced reaction. The redox behaviour of modified flat gold with AuNPs and tryptophan *via* dithiocarbamate formation indicates a substantial increase of aminoacid amount on the gold surface due to the presence of nanoparticles. The AuNPs modified with glucose oxidase and CS_2, upon gold surface attachment were also studied and their biological activity was evaluated towards glucose in the presence of a redox mediator. Atomic Force Microscopy (AFM) was used to characterize the morphology of the functionalised AuNPs and the modified electrodes.

Ackowledgements

The authors ackowledge L.M. Abrantes for helpful discussions, V. Ferreira for the synthesis of AuNPs, and to FCT for financial support: PTDC/QUI/66612/2006, PEst-OE/QUI/UI0612/2011 and Programme Ciência 2007.

References

[1] U. Saxena, M. Chakraborty, P. Goswami, Biosensors and Bioelectronics 26 (2011) 3037

[2] X. Cao, Y. Ye, S. Liu, Analytical Biochemistry (2011), doi: 10.1016/j.ab.2011.05.027

[3] C. Li , Y. Ya, G.Zhan , Colloids and Surfaces B: Biointerfaces 76 (2010) 340

[4] I. Almeida, A. C. Cascalheira, A. S. Viana, Electrochimica Acta 55 (2010) 8686

19:00 Poster 19

The Study of Physical Properties of Lipid Monolayers Composed of Amphiphilic Carotenoids

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We studied physical properties of mixed monolayers composed of dipalmitoyl-phosphatidylcholine (DPPC) and specially designed amphiphilic carotenoid (C2) containing glycerophosphocholine group. The carotenoids formed

stable monolayers at an air-water interface. Using Langmuir method we obtained series of π-A isotherms and determined the mean area per molecule of pure carotenoids (76.1 ± 2.5 Å2), DPPC (57.5 ± 4.4Å2) and for their mixtures. The C2 does not affect the shape of the isotherm and collaps pressure, but caused slight shift of the isotherm toward larger molecular area. The analysis of mixing properties showed that at the surface pressure above 10 mN/m the aggregates composed of pure carotenoids apeared, while at lower surface pressures the complexes of lipids and carotenoids were formed at relatively low molecular fraction of C2 (0.2-0.5 mol%). The compressibility modulus of the monolayers composed of DPPC was larger in comparison with those of carotenoids. However, already at low molar content of carotenoids (0,2 mol%) the elastic modulus increased suggesting high ordered structures due to van der Waals interactions between the hydrophobic chains of DPPC and polyene chain of C2. Measurement of dipole potential evidences on possibility of parallel and perpendicular orientation of C2 relatively to the subphase in the mixed monolayers.

Acknowlegements: This work was supported by Slovak Research and Development Agency (Contracts No. APVV-0410-10, LPP-0250-09 and SK-PL-0034-09) and Grant Agency VEGA (Project No.1/0794/10).

19:00 Poster 20

Conducting bipolymeric composite based on poly-pyrrole and alkoxysulfonated PEDOT. Synthesis and electrocatalytic properties

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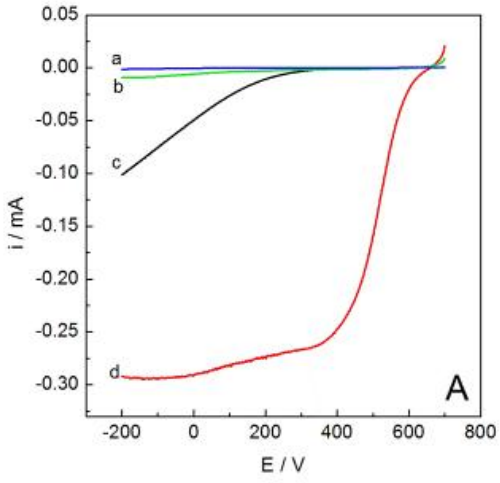
Chemical polymerization of a 3,4-ethylenedioxythiophene (EDOT) derivative bearing a sulfonate group (EDOT-S) is reported. The polymer, PEDOT-S, is fully water-soluble and has been produced by polymerizing EDOT-S in water, using $Na_2S_2O_8$ and a catalytic amount of $FeCl_3$. Thus obtained polymer can be used as doping polyanion of poly-pyrrole (PPY). Interestingly, the PPY/PEDOT-S bipolymeric composite can be synthesized in acidic aqueous solution of PY and PEDOT-S without any external oxidized. Ambient oxygen is efficient oxidizer of the binary mixture and the biopolymer forms as a dark gel after 24h in r.t. Certain cleaning produces suspensions of PPY/PEDOT-S in water or organic solvents. The cast deposits of the biopolymer on voltammetric electrodes show substantial electrochemical activity typical of conjugated conducting polymers. The acceleration of electrode kinetics at the biopolymer modified electrodes compared to the unmodified electrodes was observed for many redox systems.



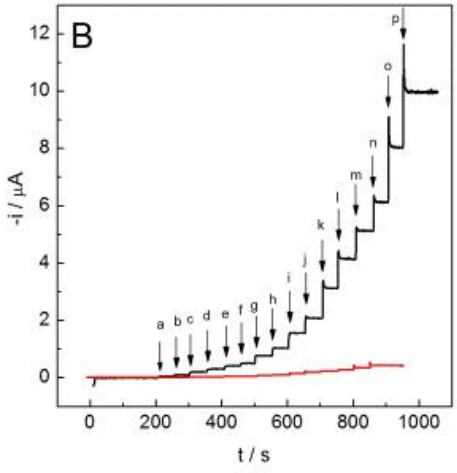


Fig. 1. (A) Linear sweep voltammograms recorded at a rotating glassy carbon electrode (1000 r.p.m.) in 0.1 M $HClO_4$ before (a) and after addition of 10 mM Fe^{3+} (b). The same experiment performed at the bipolymer-modified electrode is reflected by lines (c) and (d), respectively. Sweep rate: 2 mV s^{-1}. (B) Constant potential amperometry recorded at +0.3 V vs. Ag/AgCl at the modified rotating disk electrode (1000 r.p.m.) following addition of 2.5 (a), 5 (b), 10 (c), 15 (d), 20 (e), 25 (f), 37.5 (g), 50 (h), 75 (i), 100 (j), 150 (k), 200 (l), 250 (m), 300 (n), 400 (o) and 500 μM (p) (black line). The same experiment performed on the bare electrode is reflected by the red line.

For instance, Fig. 1A compares reductive single sweep voltammograms of Fe^{3+} cation at unmodified and biopolymer-modified electrodes. As it seen, in the latter case the voltammogram shows a clear current plateau indicating diffusion-controlled reduction reaction. Moreover, the current onset point is shifted significantly toward higher electrode potentials. This implies that the biopolymer modified electrode can be used as amperommetric sensor of Fe^{3+} ions in solution. This was experimentally verified by measuring current changes following additions of increasing concentrations of Fe^{3+} ions. The obtained current-time tracing is shown in Fig. 1B. It is evident that the observed responses are many times higher than at the unmodified electrode. The sensitivity factor calculated from the slope of the linear regression line was 0.28 μA μM cm^{-2}.

19:00 Poster 21

DNA-aptamers for thrombin detection by quartz crystal microbalance.

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Thrombin is a highly specific serine protease involved in the coagulation cascade, which converts soluble fibrinogen into insoluble strands of fibrin which is a matrix of the blood clot. The thrombin is not present in the blood under physiological conditions but appears in pathological processes including deep vein thrombosis, myocardial infarction, stroke and in central nervous system injury. Under coagulation the concentration of the thrombin in blood varied from nM to μM levels. Development of the sensitive method of the thrombin detection in nanomole level is important for clinical practice. The traditional methods of thrombin detection are based on the antigen-antibody immunoassay, clotting – based assay or synthetic-substrate-based enzymatic assays. Alternative method of thrombin detection is based on biosensors using DNA aptamers as receptors.

In this work we used thickness shear mode method to study the interaction between thromnin and DNA aptamers immobilised at the surface of quartz crystal transducer. We used 30-mer biotinylated DNA aptamer (BF) of followinh composition: 5´-GGT TGG TGT GGT TGG TTT TTT TTT TTT TTT - 3´- biotin. The immobilization of the aptamers to the surface is crucial and we compared two types of the surfaces formed on the gold electrode. First surface was formed from neutravidine on which BF was attached. Second surface was formed from the nanostructure tetrahedron DS3BT1 for oriented attachemnt of neutravidine and than for BF binding. We studied the kinetics of the changes of the series resonant frequency, f_s, and the motional resistance, R_m, of the quartz crystal transducer following addition of thrombin. We observed decrease of f_s and increase of R_m, following addition of thrombin. The changes of both parameters started already at 50 nM of thrombin.The increase of R_m suggests on increase of surface viscosity. The kinetics analysis of aptamer-thrombin system was performed. Binding experiments carried out using BF immobilized on neutravidin layer at gold surface showed that constant of dissociation is K_d = 114 nM. This constant is measure of the affinity of the interactions. The lower K_d, the higher affinity. However, lower affinity of thrombin to the aptamer was observed when DS3BT1 structures were used for aptamer immobilization (K_d =151 nM). The reasons of these differences are discussed.

Acknowledgments. This work was financially supported by Slovak Research and Development Agency (Projects VVCE-0064-07, APVV-0410-10) and by project MNT-ERA.NET II project IntelliTip (ID 431, AN 234989 to M.Š. and FFG project 823980 I.N to A.E.).

19:00 Poster 22

Structural, morphological and optical properties of $ZnAl_2O_4$ nanoparticles co-doped with Er^{3+} and Yb^{3+} prepared by combustion aerosol synthesis.

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Zinc aluminate ($ZnAl_2O_4$) is found in nature as a mineral named gahnite. This spinel presents a close-packed face-centered cubic structure belonging to the *Fd*3*m* space group, having an optical band gap of 3.8 eV, which makes it suitable for photoelectronic devices, such as plasma display panels (PDPs), and field emission displays (FEDs). In recent years, several studies have been based on $ZnAl_2O_4$ doped rare earth ions (for example: Er^{3+}, Yb^{3+}, Dy^{3+}, Tb^{3+}, Eu^{3+}, Tm^{3+}).

$ZnAl_2O_4$ co-doped $Er^{3+}$and Yb^{3+} were prepared by a combustion aerosol process. The urea and nitrate compounds dissolved in distilled water and used for the production of aerosol were injected to a high– temperature reaction zone. As results we obtained spherical nanoparticles that up-converted infrared light (980nm) to visible light (540 nm and 650 nm). The synthesized nanopowders were characterized by: TEM, SEM, XRD, PL and confocal microscopy. TEM analysis showed a broad particle size distribution for (100 - 800 nm), for $ZnAl_{1,9}Er_{0,017}Yb_{0,083}O_4$ (Er:Yb = 1:5) for the oven calcined at 990^{o}C for 3h in the air and unheated nanoparticles . Spherical polycrystalline nanoparticles were presented on the SEM photographs (Figure 1).

In order to label cellular biological structures, the up-converting nanoparticles were transported into living HeLa cells and were detected by confocal microscopy.

Our results indicate that the spinels can be visualized in HeLa cells.

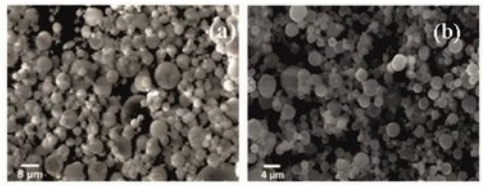

Fig. 1. SEM photographs of $ZnAl_2O_4$ co-doped $Er^{3+}$and Yb^{3+} nanoparticles (a) calcined at 990 ^{o}C for 3h in air (b) not heated.

The research was supported by the European Union within European Regional Development Fund, through grant Innovative Economy (POIG.01.01.02-00-008/08), and by the Ministry of Science and Higher Education (Poland) through Grant No. N518 424036 and Center of Excellance. The Polish National Centre for Research and Development NR13004704 and Center of Excellence

19:00 Poster 23

Electrochemical sensor based on a microarray of individually addressable chemically modified electrodes for insulin detection

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Better understanding of chemical secretion through exocytosis e.g. neurotransmitters, peptides and hormones, is of great interest for researchers in medicine, biology and pharmaceutical industry. The use of amperometry at microelectrodes makes it possible to carry out sensitive and rapid detection of exocytosis events at single cells. The combination of several individual addressable microelectrodes into an array, however, can be used to obtain spatially and temporally resolved images of exocytosis from a single cell.

We are working to develop an electrochemical sensor based on on-tip arrays of carbon fiber microelectrodes to obtain spatially and temporally resolved images of insulin secretion from a single pancreatic β-cell. Better understanding of insulin secretion from β-cells is almost certainly going to be one piece in the puzzle of unraveling diabetes mellitus, a disease that affects over 100 million people world-wide. Electrodeposition of ruthenium chloride on an array of carbon fiber microelectrodes provides a surface that can be used to catalyze the oxidation of insulin, usually electrochemically inactive. The electrochemical properties of the sensor and its surface structure have been characterized by cyclic voltammetry, square wave voltammetry, amperometry, and scanning electron microscopy. Application of the sensor to standard solutions of insulin using a flow injection system has been demonstrated.

19:00 Poster 24

Tetraazamacrocyclic copper(II) and nickel(II) complexes in host - guest systems.

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Tetraazamacrocyclic transition metal complexes depending on the properties of the components may act as a donor or an acceptor of electrons. Changing the oxidation state of the metal center by applying an appropriate potential allows to control the redox properties of the whole molecule. Depending on the redox state their complexing properties can be switched on and off.??? Our aim was to use mono- and polymacrocyclic complexes as receptors for binding guest on the surface of the electrode as well as in the solution.

Pseudorotaxane systems in the solution or on the gold surface.

The monomacrocyclic Cu(II) complex was chosen to play the role of axis of the rotaxane molecule and dibenzo-24-crown-8 to act as the ring (Fig. 1). In the first approach, both components were dissolved in the solution phase. Next, disulfide derivative of monomeric Cu(II) complex was attached to the gold substrate and the crown ether dissolved in the solution phase was the ring able to thread onto the axis. (Fig.2)

Host – guest systemsusedto bindselectedguests.

Tris – and tetramacrocyclic complexes were used to bind small guests molecules???. The interactions with two molecules: 9,10-dimethyltriptycene and fullerene, were examined.

The formation of complexes between the trismacrocyclic cyclidene hosts and π-electron-rich aromatic guests was confirmed by NMR and electrochemical studies. The 9,10-dimethyltriptycene molecule fits into the cavities formed

by the macrocyclic complex of copper and nickel . Based on the decrease of the diffusion coefficients we were able to determine the association constants of dimethyltriptycene and copper and nickel cations using the equation of Osa et al.??? and compare them with NMR results???.

For binding the molecule of C_{60}, two four-center macrocyclic compunds with short, two-carbon alkyl chains were chosen. The size of the cavity in those complexes is appropriate to accept the guest molecule. The radius of the molecule of the fullerene is approximately 7Å and the dimensions of the cavity of the macrocyclic complex is ca. 15x15Å. The changes observed in the cyclic voltammetry allowed us to confirm the formation of a new complex, which is demonstrated in the decrease of the diffusion coefficient value and in the shift of the voltammetric peaks corresponding to the redox processes of both fullerene and the metal ion center of the receptor.

???A. Więckowska, M. Wiśniewska, M. Chrzanowski, J. Kowalski, B. Korybut-Daszkiewicz, R. Bilewicz, *Pure Appl. Chem.* 2007, 79, 1077

???R. Bilewicz, A. Wieckowska, B. Korybut-Daszkiewicz, A. Olszewska, N. Feeder, K. Woniak, *J. Phys. Chem. B***2000,***104,* 11430-11434

??? T. Osa, T. Matsue, T. Fujihira, *Heterocycles*, **1977**, 6, 1833

??? J. Małecka, U. Lewandowska, R. Kamiński, I. Mames, A. Więckowska, R. Bilewicz, B. Korybut-Daszkiewicz, K. Wozniak, *Chem. Eur.J.***2011**, in press

19:00 Poster 25

Molecular imaging of lipid layers containing calixarene-cytochrome c complexes

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The vesicles and supported bilayer lipid membranes are convenient models of biomembranes. The lipid films could be modified by proteins or synthetic receptors and serve as a recognition devices for medical diagnosis. Calixarenes (CX) are being used for detection of a wide range of compounds such as metal ions, amino acids or proteins. Recently CX specific to cytochrome c (cyt c) has been developed [1]. Cyt c participates in electron transport and it is responsible for activation of the apoptotic pathway through releasing from mitochondria into the cytosol. In particularly it has been shown that cyt c induced transition of lamellar phase composed of phosphatidylcholine, which is favorable for transport of cyt c through hydrophobic part of the membrane. The detection of endogenous concentration of cyt c is of high importance for diagnosis of possible pathological processes in the organism. By atomic force microscopy we studied the topography of the self assembled lipid films composed of dimiristoylphosphatidylcholine (DMPC) contained CX and formed on freshly cleaved mica surface. The height difference between mica surface and upper part of DMPC layer was between 3 and 4 nm, which correspond to the lipid bilayer and agrees well with results published earlier. Interesting result were obtained for the layers incubated with 30 nM cyt c. The roughness of CX layer was about 5 times higher in comparison with that of DMPC, probably due to formation of monolayers and even multilayers of CX. Novel and surprising result has been obtained for mixed DMPC-CX layers at presence of cyt c. Incubation of these layers with 30 nM of cyt c resulted in transformation of rather rough multilayers into the relatively flat layers contained sharp fibers of cyt c.

Acknowledgments. This work was financially supported by Slovak Research and Development Agency (Projects VVCE-0064-07, APVV-0410-10) and by project MNT-ERA.NET II project IntelliTip (ID 431, AN 234989 to M.Š. and FFG project 823980 I.N to A.E.). We thank to Dr. T. Oshima for generous gift of CX.

[1] Oshima, T., Ishii, T., Baba, Y., Higuchi, H., Ohto, K., Inoue, K. *Solv. Extr. Res. Dev. Japan* 15 (2008), 89-98

19:00 Poster 26

Reagentless Second Generation Biosensor Free of Covalent Mediator Linking

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So-called 'second generation' biosensors are based on redox mediators aimed to deliver electrons between the enzyme active site and the electrode.

Among the advantages of the second generation oxidase-based biosensors are: operation in oxygen free media and a possibility for coulometric detection. However, because the redox mediators are small, *in vivo* leaching of the mediator is a serious concern. To eliminate this disadvantage we need to find a new method for mediator immobilization without covalent linking either to membrane forming polymer or to the enzyme.

We investigated glucose oxidase immobilization in gel of siloxanes using novel protocol based on water-organic mixtures with the high content of organic solvent reported for lactate oxidase. Obviously, to provide the mediator immobilization in such membrane the water insoluble azines were chosen. We tested unsubstituted phenothiazine, phenoxazine and their oligomers. Among them the only phenothiazine displayed electroactivity when cycled in neutral solutions.

Siloxane gels with immobilized glucose oxidase and the mediator were optimized considering concentrations of all components to provide both the highest stability and the highest response. The optimal membranes were investigated both in flow-injection system with amperometric detection and by cyclic voltammetry.

Upon the adding of glucose in solution the usual catalytic electrooxidation wave was observed. Such well-defined wave normally observed for both the enzyme and the mediator in solution, indicates diffusion ability of phenothiazine in the membrane. We noted that being water-insoluble phenothiazine was unknown as the mediator for glucose oxidase. Indeed, when immobilized a dip-coating from its organic solution phenothiazine did not show mediation ability even in the presence of both glucose and glucose oxidase in solution.

Analytical performances of the elaborated second generation biosensor based on glucose oxidase and phenothiazine immobilized into siloxane gel were investigated in flow-injection system. Sensitivity of the biosensor in FIA mode is 2 mA $M^{-1}cm^{-2}$ The lower detection limit for glucose (0.015 mM) is among the lowest ones for second generation biosensors. The linear range is from 0.05 to 50 mM glucose.

The crucial point for reagentless second generation biosensors is their operational stability. Accordingly, the latter for the elaborated biosensor was investigated. The wall-jet detector equipped with the biosensor remains its initial response (precisely, 98±1%) after 50 injections. Hence, the elaborated second generation biosensor with immobilized both the enzyme and the mediator is stable enough for multiple measurements and even can be used for continuous monitoring.

19:00 Poster 27

Properties of DODAB/oleyl alcohol and DODAB/cholesterol monolayers and bilayers

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Recently, the nanoscopic vesicular structures have been the subject of considerable interest in both: colloid and materials science. The application of liposomes is very wide and includes medicine, cosmetology, environment protection, health food formulation and production, science etc.[1] However, the high price of natural lipids strongly limits the application of liposomes. That is why it is reasonable to investigate vesicles formed with double-tailed

surfactants such as dioctadecyldimethylammonium bromide (DODAB). Unfortunately, the structures of formed vesicles were nonspherical.[2]

To improve the morphology of obtain objects the additions of oleyl alcohol and cholesterol were applied. Oleyl alcohol as the compounds possessing *cis* double bond in the chain forms liquid monolayers and therefore it can be expected that the incorporation of oleyl alcohol molecules should have strongly fluidizing influence on DODAB monolayer. The effect of cholesterol on membranes is in turn rather complex. Generally cholesterol reduces the fluidity of bilayers and monolayers but the addition of small amount of this sterol to dialkyldimethylammonium bromides monolayers may also cause an increase of their fluidity.[3]

It is suggested that at the surface pressures between 30 and 35 mN/m the monolayer properties, such as area per molecule, lateral pressure and elastic compressibility modulus, correspond to the properties of bilayer[4],[5] that is why in this work Langmuir monolayer measurements of the DODAB/oleyl alcohol and DODAB/cholesterol mixtures were performed.

References:

[1] D. D. Lasic; *Handbook of Biological Physics*, chapter 10: *Applications of Liposomes*, Elsevier Science B.V., California, **1995**

[2] M. Kepczynski, J. Lewandowska, K. Witkowska, S. Kędracka-Krok, V. Mistrikova, J. Bednar, P. Wydro, M. Nowakowska; *Chemistry and Physics of Lipids,***2011**, *164*, 359

[3] K. Hąc-Wydro, P. Wydro, P. Dynarowicz-Łątka; *Journal of Colloid and Interface Science*, **2005**, *286*, 504

[4] D. Marsh; *Biochim. Biophys. Acta*, **1996,***1286,* 183

[5] J. F. Nagle, S. Tristram-Nagle; *Biochim.Biophys. Acta*, **2000,***1469*, 159

19:00 Poster 28

3D bioarchitectures constructed on carbon cloth for the development of biofuel cells

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Powering future generations of implanted medical devices by harvesting energy from the human body became a challenge of the last decades. Glucose-based biofuel cells appear to be the most promising approach since they produce electrical energy from glucose and oxygen. These two substrates are present in physiological fluids. However, such biofuel cells are limited by the difficult electrical wiring of enzymes and their poor adhesion to the electrodes. Different strategies were proposed to solve these problems such as wiring enzymes with redox active species using mechanical confinement, Os-complex containing redox polymers**[1]** and (or)nanomaterials**[2]**. Carbon nanotubes were widely used due to their specific properties in terms of increased surface area and high electric conductivity. Moreover, carbon nanotubes are known for their high chemical and electrochemical stability facilitating the electron transfer between the active site of enzymes and the electrode surface. Carbon nanotubes were, thus deposited on different kind of materials to improve the matrix conductivity and the electron transfer properties.

In this context and with the aim to design a new generation of biofuel cells, we report an original 3 D nanostructure based on carbon nanotubes directly grown on a carbon cloth allowing an efficient immobilization of biological recognition elements. We combined the excellent properties of the carbon nanotubes with those of the carbon cloth to offer highly porous three-dimensional nanostructured frameworks. Results using a variety of different enzymes were immobilized on this support material and investigated with respect to their properties as biofuel cell anodes and cathodes. Moreover, results of complete biofuel cells based on these electrodes will be presented.

[1] L.Stoica, N.Dimcheva, Y.Ackermann, K. Karnicka, D.A.Guschin, P.J.Kulesza, J.Rogalski, D.Haltrich, R.Ludwig, L.Gorton, W.Schuhmann, *Fuel Cells***9**(2009) 53

[2] A.Zebda, C.Gondran, A.Le Goff, M.Holzinger, P.Cinquin, S.Cosnier, *Nature Comm.***2**(2011) 370

19:00 Poster 29

Electrochemical uranyl biosensor with DNA oligonucleotides as receptor layer

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Rapid and accurate methods allowing for detection of trace level of uranyl ion can be employed for environmental, geochemical or health safety applications. According to literature, at certain pH values uranyl has a strong affinity to phosphate residues. This mechanism was used in various electrochemical sensors for uranyl ion determination, with the recognition layer composed of: 2-mercatpoethanol/$POCl_3$, cysteamine/ 2-aminoethyl dihydrogen phosphate or (t-butylphenyl)-N,N-di-(isobutyl) carbamoylmethylphosphineoxide [1-3]. The uranyl ion detection limit for the last of above-mentioned sensor is at parts per million level. Nevertheless, the analytical procedure in this case was very complicated.

It was recently found out in our laboratory that recognition layer of short DNA oligonucleotides, formed on gold electrode, can be very useful for electrochemical uranyl detection. After subjection to sample solution containing uranyl ion (UO_2^{2+}), the electrochemical properties of DNA layer changes. This can be quantified using an electrochemical marker (e.g. methylene blue). This approach allows for trace level determination of uranyl ion. Moreover, impedance spectroscopy can be employed to further lower the detection limit.

To evaluate the influence of pH on DNA-uranyl interactions, the Quartz Crystal Microbalance (QCM) measurements were conducted. The gold transducer was modified with single stranded DNA and subsequently subjected to uranyl solutions of different pH values. The decrease in transducer oscillation frequency corresponds to interactions of uranyl ions with ssDNA phosphate residues. The strongest DNA-uranyl interaction was observed at pH 5.0.

It is well known that uranyl has cleaving effect on DNA strands [4,5]. However, we did not noticed this during QCM tests. To further explore this problem, capillary electrophoresis experiments were performed. No degradation of oligonucleotide upon prolonged contact with uranyl ion solution was observed, thus it was concluded that proposed recognition monolayer can be utilized for preparation of uranyl ion sensors.

ACKNOWLEDGMENT

This work was co-financed by the Polish Ministry of Science and Higher Education (research project N N204 125237) and Warsaw University of Technology.

[1] A. Becker, H. Tobias, D. Mandler, *Anal. Chem.***2009**, 81, 8627.

[2] R. Banerjeea, Y. Katsenovichb, L. Lagosb, M. Sennc, M. Najad, V. Balsamoe, K. H. Pannellc, Ch. Li, *Electrochim. Acta.***2010,** 55, 7897

[3] R. K. Shervedani, S. A. Mozaffari, *Surf. Coat. Tech.***2005,** 198, 123

[4] P. E. Nielsen, C. Jeppesen, O. Buchardt, *Febs Lett.***1988**, 235, 122

[5] M. Yazzie, Sh. L. Gamble, E. R. Civitello, D. M. Stearns, *Chem. Res.Toxicol.***2003**, 16, 524

19:00 Poster 30

Planar microsensors based on phenylboronic acid Self-Assembled Monolayers

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Electrochemical sensors found many applications as simple and selective analytical devices allowing fast and low-cost analysis in clinical diagnostics, environmental and process monitoring without the necessity of sample preparation. Their selectivity is mainly governed by the analyte recognition process – selective complexation of the analyte by the receptor molecules – occurring in the receptor layer. Therefore, the development of novel sensors requires the synthesis of selective receptors which could be introduced into polymeric films or immobilized on the surface of the transducers to form selective receptor layers.

Phenylboronic acid derivatives are widely used as selective receptors for developing new analytical methods for the determination of bioanalytes such as: sugars, neurotransmitters and some anions. Their high stability and especially their ability of fast and reversible ester formation with 1,2- and 1,3-diols have been applied to detect saccharides in solution (homogenous methods) as well as to design new optical saccharide sensors. In such approaches, fluorescent phenylboronic acids are usually applied to signal the binding process. Moreover, thiol-modified phenylboronic acids can be immobilized directly on the gold surface and form a self-assembled monolayer, acting as receptor layer of electrochemical sensors sensitive to sugars [1].

In this report, preliminary studies on the fabrication of electrochemical microsensors based on phenylboronic acid self-assembled monolayers of 4-mercaptophenyloboronic acid (MPBA) are presented. The efficiency of the formation of MPBA monolayers on the surface of back-side contact gold microelectrodes developed in silicon technology were studied using quartz crystal microbalance and chosen electrochemical techniques (cyclic voltammetry, impedance spectroscopy). Finally, the responses of the phenylboronic acid monolayer-modified microsensors towards selected bioanalytes (fluoride anion) have been reported.

[1] Takahashi S., Anzai J., *Langmuir* 21 (2005) 5102-5107

Acknowledgment

This work has been supported by the European Union in the framework of European Social Fund through the Warsaw University of Technology Development Programme, realized by Center for Advanced Studies and by National Center for Research and Development within a framework of LIDER programme (Nr LIDER/17/202/L-1/09/NCBiR/2010) and by Project MNS-DIAG Nr POIG.01.03.01-00-014/08-00.

19:00 Poster 31

Exploitation of electrospun and solution blown three-dimensional carbon fiber nonwovens for microbial bioelectrocatalysis

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Microbial bioelectrochemical systems (BES) represent an upcoming technology for the exploitation and cleaning of waste water.[1] In addition, BES are gaining importance as bio-analytical devices like microbial fuel cell (MFC)-type sensors, e.g. for BOD in waste waters as well as for the analysis of microbial activity.[1,2] In BES, microorganisms are used as biocatalysts at the anode allowing the interception of electrons released during the oxidation of substrates. During the past decade, the average current densities of the biofilm anodes have already impressively increased from microampere per square cm level to between 0.7 and 1 mA cm^{-2}. Since the improvement of the biological component in BES becomes increasingly difficult, the improvement of the electrode materials becomes an important task. One strategy is the improvement of the electrode surface properties by surface treatment procedures such as ammonia treatment, polymer modification or surface oxidation.[3,4] Another promising path is to increase the active surface area by means of, e.g., brush or fiber electrodes[5,6] and 3D electrode materials - a path that already delivers promising results (about 2.4 mA cm^{-2})[7]. The aim of the presented work was to exploit high surface area electrospun and solution blown fiber materials to enhance the microbial bioelectrocatalysis at BES anodes. Herein, three-dimensional electrospun and solution-blown carbon fiber nonwovens are shown to be excellent and promising anode materials for mi-

crobial BES such as MFCs. They combine the use of a minimum amount of carbon and great performance. The bioelectrocatalytic anode current density values reached up to 3 mA cm^{-2}, which represents to date, amongst the highest reported values for electrocatalytically active biofilms of *Geobacter sulferreducens*.[8] These current densities were achieved without chemical surface modification, which may represent an advantage with respect to longevity. Based on this initial study, further and systematic investigations are proposed to fully exploit the potential of this class of materials. A special emphasis of further investigations must be on tests designed to elucidate the long-term behavior of these electrode materials and the resistivity against clogging of the pore structures.

References:

[1] K. Rabaey *et al.* (Eds.), Bioelectrochemical Systems: From Extracellular Electron Transfer to Biotechnological Application*, IWA Publishing* 2009.

[2] D. Odaci *et al.,Bioelectrochem.* 2009, 75, 77-82.

[3] S. Cheng *et al., Electrochem. Comm.* 2007, 9, 492-496.

[4] X. Wang *et al., Environ. Sci. Technol.* 2009, 43, 17, 6870-6874.

[5] B.E. Logan *et al., Environ. Sci. Technol.* 2007, 41, 3341-3346.

[6] Y. Liu *et al., Biosens.Bioelectron.* 2010, 25, 2167-2171.

[7] Y. Zhao *et al.,Chem. Eur. J.* 2010, 16, 4982-4985.

[8] S. Chen *et al.,Energy Environ. Sci.* 2011, 4, 1417-1421.

19:00 Poster 32

Electrochemically synthesized molecularly imprinted polymer for determination adenosine 5'-triphosphate (ATP)

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Sensitive to the adenosine 5'-triphosphate (ATP) nucleotide tailor-made molecular cavities were imprinted in a thiophene polymer network to devise and fabricate a novel chemical sensor for determination of ATP. A molecularly imprinted polymer (MIP) as a selective recognition material of the chemosensor was prepared by potentiodynamic electropolymerization. Three different functional monomers were used for complexation of one ATP molecule. The uracil substituent of bis(2,2'-bithien-5-yl)methane complementary paired the adenine moiety of the target nucleotide analyte. Besides, the boronic acid of reversibly bound vicinal diol of the ribofuranose moiety. Three phosphate groups of ATP in their anionic forms, were bound with hydrogen bonds to the amide moiety of bis(2,2'-bithien-5-yl)methane. In order to probe the effect of different binding motifs adopted in the present ATP recognition and to visualize the structure of the supramolecular complex formed, DFT calculations at the B3LYP/6-31G(d) level were performed. The signal transducer of this chemosensor was a 10 MHz quartz crystal resonator of an electrochemical quartz crystal microbalance (EQCM) and a Pt disk electrode for the piezoelectric microgravimetry and capacitance determination, respectively, under flow-injection analysis conditions. Properties of the MIP film were unravelled by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy.

19:00 Poster 33

Electroanalytical system based on lactate biosensor with preliminary concentration for non-invasive diagnostics

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Lactic acid is one of most studied analytes. Its concentration is an important parameter in clinical diagnostics and sport medicine [1]. Various methods using different types of sensors based on lactate oxidase (LOD) have been proposed for the determination of lactate concentration in solutions.

Increasing demand for non-invasive methods for metabolites determination in human fluids resulted in extensive research of exhaled breath condensate (EBC) [2]. However, some components of EBC may affect the results of the lactate determination.

Lactate biosensors based on screen-printed electrodes modified with Prussian blue were developed [3]. LOD was immobilized on the surface of working electrodes into polymer membrane containing high percentage of organic solvent. The biosensor was used for the lactate determination in flow injection analysis (FIA) techniques. It was showed that lactate could be measured over a dynamic range of 2-1000 μM which was linear up to 200 μM. The highest corresponding sensitivity was 0.17 A/M•cm^2. The lower detection limit was 0.8 μM. The response time was 30 seconds. The obtained results of the lactate determination in real objects were comparable to the measurements performed with automated Biosen C-line (Germany).

The developed lactate biosensor was used in FIA techniques with preliminary concentration. The ion-exchange column was filled with silica phase with quaternary amine groups providing a strong anion-exchange mechanism of retention. Thus the influence of hydrogen peroxide is eliminated. Moreover, the sensitivity went up by a factor of fifty and the highest one was 8.1 A/M•cm^2. The lower detection limit was 0.02 μM.

The developed electrochemical system was applied to the lactate determination in EBC (120 samples) collected from healthy patients before and after physical exercise as well as from patients suffering from different pulmonological diseases. The increasing of lactate concentration in EBC during physical exercise was shown.

Acknowledgments

The authors are grateful to the Research Institute for Pulmonology and the Research Institute for Physical Culture and Sport for providing the samples of EBC. Also we acknowledge the financial support from Russian Ministry of Science and Education, project №14.740.11.1374.

References

1. Sakharov D. A., Shkurnikov M. U., Vagin M. Yu., Yashina E. I., Karyakin A. A., Tonevitsky A. G. Relationship between lactate concentrations in active muscle sweat and whole blood. // Bulletin of Experimental Biology and Medicine, 24 Nov 2010, pp. 1-3.

2. Gessner C., Wirtz H. Continuous exhaled breath condensate measurements in ventilated patients. // Resp. Care. 2006, V. 51, pp. 1118-1119.

3. Yashina E.I., Borisova A.V., Karyakina E.E., Shchegolikhina O.I., Vagin M.Yu., Sakharov D.A., Tonevitsky A.G., Karyakin A.A. Sol-gel immobilization of lactate oxidase from organic solvent: toward the advanced lactate biosensor. // Anal. Chem. 2010, 82, pp. 1601-1604.

19:00 Poster 34

Effect of deglycosylation of cellobiose dehydrogenase applied to 3rd generation biosensors and biofuel cells

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Cellobiose dehydrogenase (CDH) is an extracellular highly glycosylated two domain redox enzyme, which is one of the very few redox enzymes that shows direct electron transfer (DET) properties with electrodes. The catalytically active domain contains flavin adenine dinucleotide (FAD) and the other contains heme *b*. For the native glycosylated enzyme only the heme domain shows DET properties reflected by that the redox conversion of the heme group is shown in cyclic voltammetry (CV). For the native enzyme DET of the FAD domain is not show. Recently we initiated studies of deglycolysated CDH aiming at obtaining more efficient DET properties in line with previous reports for horseradish peroxidase [1,2] and glucose oxidase [3]. *Ceriporiopsis subvermispora* (*Cs*) and *Phanerochaete chrysosporium* (*Pc*) CDH were used in this study. When deglycosylated CDH was used instead CV revealed signals from both the heme and FAD. However, in the presence of substrate catalytic currents in CV only emanate at potentials close that of the heme for both CDHs.

When investigated adsorbed on graphite electrodes *Cs*CDH (16% glycosylation) its deglycosylated equivalent shows at least 3 times as high catalytic currents as its glycosylated counterpart. *Pc*CDH (9% glycosylation) shows twice higher currents for its deglycosylated form. A similar behavior is observed on thiol modified gold electrodes for *Cs*CDH but not for *Pc*CDH. In this last case both the glycosylated and deglycosylated variants show equally high catalytic currents. The improvement in current response on graphite is due to a higher amount of deglycosylated enzyme immobilized on the graphite electrode. The basic bioelectrochemistry as well as the bioelectrocatalytic properties will be shown as well as applications of CDH modified electrodes as 3rd generation biosensors and as bioanodes in biofuel cells.

[1] G. Presnova, V. Grigorenko, A. Egorov, T. Ruzgas, A. Lindgren, L. Gorton, T. Börchers, Faraday Discus., 116 (2000) 281-289.

[2] E. E. Ferapontova, V. G. Grigorenko, A. M. Egorov, T. Börchers, T. Ruzgas, L. Gorton, Biosens. Bioelectron., 16 (2001) 147 - 157.

[3] O. Courjean, F. Gao, N. Mano, Angew. Chem. Int. Ed., 2009, 48, 5897 –5899.

This work was financially supported by the European Commission, “3D-Bionanodevice” NMP4-SL-2009-229255.

19:00 Poster 35

Direct electron transfer of Trametes hirsuta laccase in a dual-layer-architecture of poly(3,4-ethylenedioxythiophene) films

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Laccase (EC 1.10.3.2) widely distributes in fungi, higher plants, and also in some bacteria, which has a relatively broad substrate spectrum and is thermostable and environmentally friendly catalyst. Laccase finds application as the catalyst in the O_2-consuming cathode for biofuel cells after being integrated into the enzyme electrode [1, 2].

Direct electron transfer (DET) type biocatalysis was accomplished for *Trametes hirsuta* laccase (*ThL*) on glassy carbon (GC) electrode by immobilizing laccase into a well-designed dual-layer-architecture of poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT films were subsequently deposited on GC electrode *via* electropolymerization, with NO_3^- as counterion for the first accommodation layer and poly(styrene-sulfonate) anions (PSS^-) for the second capping layer. The enzyme (*ThL*) was cast on top of the accommodation layer (PEDOT-NO_3), and then the capping layer (PEDOT-PSS) was electrodeposited to entrap *Th*L between the layers. This enzyme electrode is reported to be able to promote DET between *Th*L and the GC electrode and catalyze the reduction of O_2 into water. The influence of fabrication parameters on the enzyme electrode performance was investigated through chronoamperometric measurements. The investigated parameters included different combinations of PEDOT films, *Th*L loading and the thicknesses of both PEDOT layers. As a representative, one optimized dual-layer-architecture enzyme electrode of PEDOT-NO_3(28 mC)/*Th*L(1.26 U)/PEDOT-PSS(3.5 mC) performed fairly good reproducibility and operational-stability. Its pH-profile exhibited a bell-shape with an optimal pH in the range of 3.0-3.5. The influences of ionic strength and addition of a non-ionic surfactant into the buffer solution on the enzyme electrode performance were also studied in order to obtain information about DET-mechanism of *Th*L in the dual-layer-architecture. Based on the information obtained from different characterizations, π-π interaction between the PSS^- ions and the hydrophobic substrate-binding pocket in the vicinity of the T1 Cu site was proposed to result in a favorable location of the conducting polymer chain close to the T1 Cu site and thus facilitate DET of *Th*L within this particular architecture [3]. The applicability of this approach to various electrode materials is also underlined, which makes it a favorable approach to construct an O_2-consuming cathode for biofuel cells.

References

[1] Barton, S.C., Gallaway, J., & Atanassov, P., **Chem. Rev.**, 104 (**2004**) 4867-4886.

[2] Shleev, S., Tkac, J., Christenson, A., Ruzgas, T., Yaropolov, A.I., Whittaker, J.W., & Gorton, L., **Biosens. Bioelectron.**, 20 (**2005**) 2517-2554

[3] Wang, L., Latonen, R.-M., Sjöberg-Eerola, P., Eriksson J.-E., Bobacka, J., Boer, H., & Bergelin, M., **J. Phys. Chem. C**, 115 (**2011**) 5919-5929

19:00 Poster 36

PEDOT/Lignosulfonate polymer composites: synthesis and electroanalytical application

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3,4-ethylenedioxythiophene (EDOT) was electropolymerized in the presence of sodium lignosulfonate (LS) at constant current density of 0.25 mA cm^{-2}. As a result, a thin composite film consisting of poly(3,4-ethylenedioxythiophene) and LS (PEDOT/LS) was deposited on the electrode surface. Unlike PEDOT, PEDOT/LS shows appreciable redox activity due to LS-derived quinone moieties (Fig. 1A) with diffusion-like charge propagation across the film thickness. We used pulsed chronoamperometry to determine the apparent charge transport diffusion coefficient and we found that for at sufficiently short times the current decay response conforms to the Cottrell equation. From this dependence, for the film polymerized at 50 mC cm^{-2} we found the D_{ct} value to be 1.6×10^{-9} cm^2 s^{-1}. The film-modified gold electrodes can be used as voltammetric sensor of uric acid (UA) in the presence of ascorbic acid (AA). Interestingly, the UA response is catalysed by the presence of AA and for high AA/UA concentration ratios more that 10-fold enhancement of the UA peak currents are apparent (Fig. 1B).

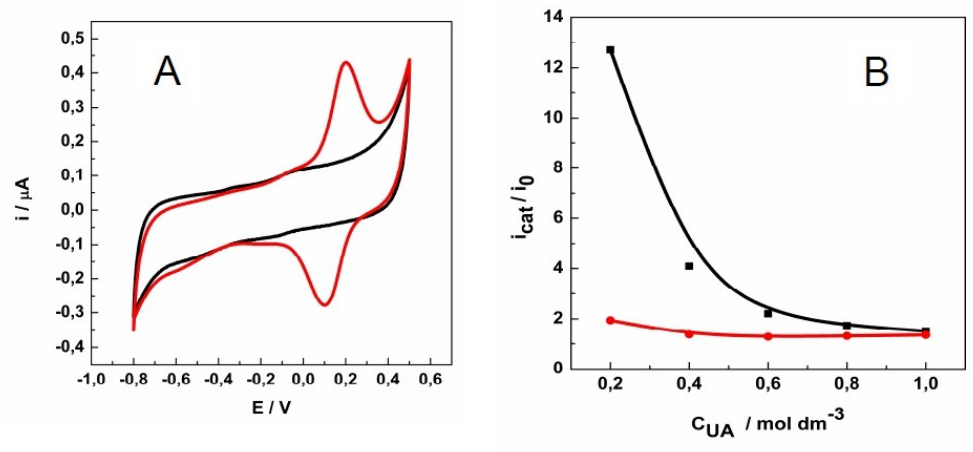

Fig. 1 (A) Comparison of cyclic voltammograms of PEDOT films electropolymerized in the absence (black line) and presence of LS (red line). LS concentration in the plating bath – 1 mg cm^{-3}. Scan rate – 10 mV s^{-1}. Electrolyte – phosphate buffer (pH 7.4). (B) AA-induced peak current enhancement of UA on PEDOT/ClO4 (red line) and PEDOT/LS film (black line) as a function of UA concentration.

Works are in progress to evaluate the performance of the proposed composite toward electrochemical sensing of other biomolecules.

Acknowledgement This work was financially supported by Polish Ministry of Science and Higher Education under project No N N209 450939.

19:00 Poster 37

Ascorbic acid-oxygen biofuel cell and zinc-oxygen cell based on carbon-silicate biocathode

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In last few years attention is paid to construction of implantable power sources for medical devices [1]. These are miniature biofuel cells or hybrid cells, where enzymes are applied as catalyst of electrodes reaction and physiological fluids perform fuel function [2,3]. In such case size of cell is limited only by size of anode and cathode. The most popular example is glucose-oxygen biofuel cell [4].

Here, we would like to present biofuel cell operates on ascorbic acid oxidation and dioxygen reduction and hybrid cell with zinc anode [5]. Both devices consist of carbon-silicate biocathode obtained from hydrophilic carbon nanoparticles and functionalized silicate particles [6] or film [7] further modified with adsorbed bilirubin oxidase. The new carbon-silicate materials were obtained employing the layer-by-layer method [8]. The electrode applied as cathode in ascorbic acid-dioxygen biofuel cell was covered by Nafion to prevent bilirubin oxidase deactivation. The same carbon-silicate material was also used as bioanode for ascorbic acid oxidation.

The electrodes were examined by cyclic voltammetry, chronoamperometry and Scanning Electron Microscopy. Their properties clearly depends on the amount of carbon-silicate material deposited on the substrate. In particular nanoparticulate material significantly decrease overpotential of ascorbic acid oxidation. This allows to construct the model of ascorbic acid-oxygen biofuel cell and determine current-voltage characteristics for both types of batteries.

References

[1] Heller A., Phys. Chem. Phys. 6 (2004) 209.

[2] Heller A., Anal. Bioanal. Chem. 385 (2006) 496.

[3] Barton S.C., Gallaway J., Atanassov P., Chem.Rev. 104 (2004) 4867.

[4] Cinquin P., Gondran C., Giroud F., Mazabrard S., Pellissier A., Boucher F., Alcaraz J-P., Gorgy K., Lenouvel F., Mathe S., Porcu P., Cosnier S., PlosOne 5 (2010) e10476.

[5] Nogala W. Celebanska A., Wittstock G., Opallo M., Fuel Cells 10 (2010) 1157.

[6] Celebanska A. Tomaszewska D., Lesniewski A., Opallo M., Biosens. Bioelectron. 26 (2011) 4417.

[7] Szot K., Leśniewski A., Niedziolka J., Jonsson M., Rizzi C., Gaillon L., Marken F., Rogalski J., Opallo M., J. Electroanal. Chem 623 (2008) 170.

[8] Crespilho F., Zucolotto V., Oliveira Jr.O., Nart F. Int. Electrochem. Sci. 1 (2006) 194.

19:00 Poster 38

Electrochemical observation of the thermally induced phase transition for a switchable polymer immobilised onto gold electrodes

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One of the most efficient methods for solid surface refinement is modification with thin organic polymer films. A very promising class of polymers for such surface modifications is the group of so called switchable polymers. These macromolecular compounds undergo very sharp reversible phase transitions in response to external stimuli such as light irradiation or temperature and enable so a simple way for rapid variations of surface properties, for example wettability. Different non-electrochemical methods have already been used in investigating switching phenomena of thermoresponsive polymers on solid surfaces. In this study it is shown how the structural changes in the polymer film on gold electrodes can be followed by electrochemical means.

For this purpose a thermally switchable polymer (copolymer of 2-(2-methoxyethoxy)ethyl methacrylate, oligo(ethylene glycol) methacrylate and 3-(2-methyl-acryloylamino)-propyl-ammonium chloride) with a lower critical solution temperature (LCST) around 38 °C was prepared and covalently bound to the surface of gold wire electrodes. Subsequently cyclic voltammetric and impedimetric measurements with so prepared working electrodes were realised in aqueous potassium ferro-/ferricyanide solutions at different temperatures. The results of these studies show successful immobilisation of the polymer on the surface of gold, since the interfacial impedance is clearly enlarged with the polymer film present on the surface (increased resistance and decreased capacitance). Furthermore, significant changes of the temperature dependence of the voltammetric peak current and the peak separation values at LCST clearly demonstrate the thermally induced phase transition on the gold surface. Thus, first results can be presented, showing the potential usefulness of electrochemical methods to follow structural polymer changes on surfaces.

19:00 Poster 39

Electron transfer studies with different sugar oxidizing enzymes and osmium polymers to improve the current density

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Glucose dehydrogenase (GDH) from *Glomerella cingulata*(*Gc*GDH, EC 1.1.99.10) is an extracellular redox enzyme. The native enzyme is a monomeric glycosylated polypeptide and has one non-covalently bound flavin adenine dinucleotide (FAD) molecule acting as the redox cofactor. Pyranose dehydrogenase from *Agaricus meleagris* (*Am*PDH, EC 1.1.99.29) is an extracellular redox enzyme. The native enzyme is a monomeric glycosylated polypeptide and has a molecular mass of 66,547 Da, containing 7% carbohydrates and one covalently bound flavin adenine dinucleotide (FAD) molecule acting as the redox cofactor. PDH can oxidise its substrate at the C-1, C-2 or C-3 as well as perform double oxidation at C-1,2, C-2,3 and it has no anomeric specificity [1].

This new extracellular redox enzyme, flavin adenine dinucleotide (FAD) dependent glucose dehydrogenase from *Glomerella cingulata*(*Gc*GDH) was electrochemically studied to catalyze the oxidation of glucose on spectrographic graphite electrode. Six Os polymers, whose redox potentials are ranged in a broad potential window between +15 and +489 mV vs. NHE, were used to "wire" the *Gc*GDH on spectrographic graphite electrodes for possible applications in biosensors and biofuel cells. [2, 3]. The *Gc*GDH/Os-polymer modified electrodes were evaluated in a chronoamperometric mode using FIA. The current response was investigated under a step-wisely increased potential window. The performance of the redox polymers for enzyme wiring was investigated using glucose as substrate. The current response was investigated under a step-wisely increased potential window. The ratio between GDH:Os-polymer was optimized. It was observed that the ratio between GDH:Os-polymer in the overall loading of the enzyme electrode significantly affects the performance of the enzyme electrode on catalyzing the glucose oxidation. The best Os-polymer had a potential of +309 mV vs. NHE and *Gc*GDH:Os-polymer ratio was 1:2 yielding a maximum current density of 493 μAcm^{-2} for 30 mM glucose was produced by the *Gc*GDH/Os c modified electrode.

After characterization of *Gc*GDH, we coimmobilized equal units of *Gc*GDH with *Am*PDH enzymes along with Os-polymer c on graphite electrodes to improve the current density. With this coimmobilization of both enzymes, we were successfully able to improve the current density. The reason for this improvement is that *Am*PDH enzyme also can oxidize the products of *Gc*GDH enzyme due to its ability to oxidize at C-1, C-2 or C-3 as well as doubleoxidation at C-1,2, C-2,3.

References

[1] C.K. Peterbauer, J. Volc, Pyranose dehydrogenases: biochemical features and perspectives of technological applications, Appl. Microbiol. Biotechnol., 85 (2010) 837–848.

[2] Muhammad Nadeem Zafar, Federico Tasca, Susan Boland, Magdalena Kujawa, Ilabahen Patel, Clemens K. Peterbauer, Donal Leech, Lo Gorton, "Wiring of pyranose dehydrogenase with osmium polymers of different redox potentials", Bioelectrochemistry, 80: 38-42 November 2010.

[3] F. Mao, N. Mano, A. Heller, Long tethers binding redox centers to polymer backbones enhance electron transport in enzyme "wiring" hydrogels, J. Am. Chem. Soc. 125 (2003) 4951–4957.

19:00 Poster 40

Biofuel cell based on arylated carbon nanotubes

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Construction of an efficient electrode for a biofuel cell and hybrid devices powered by external fuel is the aim of our study. We focus on the development of an efficient cathode for the electroreduction of dioxygen using laccase and modified carbon nanotubes[1,2]. In our study, single-walled carbon nanotubes (SWCNTs) were covalently modified with arylated group (anthraquinone, anthracene, aniline, terphenyl, naphthalene) and used for the construction of cathodes for biocatalytic reduction of dioxygen. The nanotubes with aromatic groups casted onto the electrode increased the working surface of the electrode and enabled efficient direct electron transfer (DET) between the enzyme and the electrode. The catalytic current density, potential and stability in time were compared for all of these electrodes, and the electrode showing the best properties was tested in a hybrid cell with Zn anode and in an enzymatic fuel cell with glucose dehydrogenase based anode.

References

1. K. Stolarczyk, E. Nazaruk, J. Rogalski, R. Bilewicz, Electrochim. Acta 53 (2008) 3983.

2. K. Sadowska, K. Stolarczyk, J.F. Biernat, K.P. Roberts, J. Rogalski, R. Bilewicz, Bioelectrochem. 80 (2010) 73.

19:00 Poster 41

Oligonucleotide and aptamer derivatized surfaces in potentiometric sensors: preliminary results

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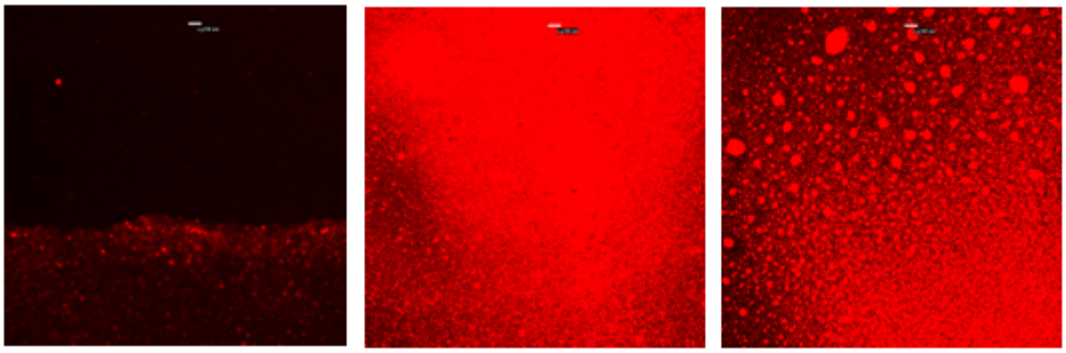
In genetic molecular diagnostics there is a big need for instruments to detect different DNA variations and mutations selectively and fast to diagnose the human genetic disorders. The current methods are usually based on fluorescence. They are often expensive and time-consuming and in addition they are not always appropriate for high throughput multiplex analysis. Amperometric DNA sensors are in the scientific research stage. Potentiometric DNA sensors have been investigated much less in this respect.

In the present study, oligonucleotides and aptamers were covalently coupled to carboxylated PVC based potentiometric sensor coatings. Oligonucleotides are multiply charged molecules which we found earlier to have unexpectedly good detectability on non-selective anion sensitive sensors.

Aminated DNA was coupled to a carboxylated PVC membrane. On the attached figure we see a blank membrane on the left (negative control), a membrane with covalently coupled aminated DNA with fluorophore (Cy3) in the middle (positive control) and a membrane with covalently coupled aminated DNA on the right (experiment). The complementary DNA with fluorophore (Cy3) was added to hybridize in 0,01M MES to each membrane. The hybridization was checked with a confocal microscope.

We already investigated the effect of sensor kinetics and sensor response for e.g. dopamine selective aptamer based sensors and compared it to the behavior of non-derivatized sensors.



Sunday, 6 November

Breakfast
Sunday morning, 6 November, 8:00

Morning Session 1
Sunday morning, 6 November, 9:00
Chair: Bilewicz and Wollenberger

9:00 Tutorial lectore

Potentially implantable bioelectronic devices for biosensing and biofuel cell applications

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The fabrication and characterisation of potentially implantable bioelectronic devices,[1] *e.g.*, biosensors and biofuel cells, is important for different biomedical applications. Since the topic delineated in the title is very broad the lecture will mostly be focused on glucose sensitive amperometric biosensors and glucose/oxygen biofuel cells operating in human physiological fluids. Nowadays these devices have been designed for and tested in both *in vitro* and *in vivo* situations,[2-5] and also practically exploited.[6-7]

Firstly, major classifications of biodevices will be described and basic mechanisms of their function including useful mathematical apparatus will be given. Secondly, historical aspects on their fabrication, investigation, and application will be presented.[8-10] This would include recently designed biodevices based on nanotechnological achievements, which were characterised in detail with the help of surface electrochemistry, ellipsometry, AFM, and SEM. During the lecture significant attention will be also devoted to proper surfacemodification procedures to produce bionano-strucutres serving as sensitive, linear, and stable biosensors, as well as bioanodes and biocathodes of efficient and stable biofuel cells. Finally, further perspectives in the field of potentially implantable bioelectronics will be discussed.

1. E. Katz. *Electroanalysis*, 2006, 18, 1855
2. D. Gough et al. *Science Translational Medicine*, 2010, 2, 42
3. V. Coman et al. *Fuel Cells*, 2010, 10, 9

4. P. Cinquin et al. *PLoS One*, 2010, 5, 5
5. A. Zebda et al. *Nature Communications*, 2011, DOI: 10.1038/ncomms1365
6. E. Dassau et al. *Diabetes Care*, 2010, 33, 1249
7. E. Cengiz et al. *Expert Review of Medical Devices*, 2011, 8, 449
8. M. Beltzer and J. Batzold. *Proc. Intersoc. Energy Convers. Eng. Conf.*, 4th, 1969, 354
9. S. Barton at al. *Chemical Reviews*, 2004, 104, 4867
10. A. Heller. *Physical Chemistry Chemical Physics*, 2004, 6, 209.

The work has been supported financially by the European Commission (FP7 project NMP4-SL-2009-229255) and the Swedish Research Council (project 2009-3266).

9:40 Keynote lecture

Development of multifunctional bioelectrocatalytic films for oxidation of ethanol

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The main goal of our research was to design, characterize and evaluate of utility distinct dehydrogenase containing multi-component bi-enzymatic and well organized bioelectrocatalytic systems capable of effective oxidation of ethanol in neutral media.

In our work, we have exploited unique characteristics of multi-walled carbon nanotubes (CNTs) [1,2] to construct the efficient anodic bioelectrocatalytic system of potential utility for biofuel cells and biosensors. Some attention has been also paid to the choice of the modifying agent poly(diallyldimethylammonium chloride) (PDDA) used to stabilize CNTs. While PDDA seems to form stable ultra-thin layers on CNTs, it is not expected to serve as a good charge (electron) mediator but it is reasonable to expect that PDDA would interact or attract electrostatically with negatively charged sites of the enzyme (or combination of dehydrogenase enzymes). Our highly porous CNT-based films have presumably acted as three-dimensional network of nanowires around the enzyme molecules and have promoted the efficient electron transfer. On the whole, combination of PDDA-modifed MWCNTs and two distinct dehydrogenase enzymes within the film has produced a catalytic system capable of oxidation of ethanol at fairly low potentials (ca. 0.1 V vs Ag/AgCl). Kinetic parameters including heterogeneous rate constants at different applied potentials as well as an apparent Michaelis-Menten constant ($K_M^{app} \sim 0.33$ mM) were also determined. Among important issues are good stability and reproducibility of responses both under voltammetric and amperometric conditions.

References

[1] B. Kowalewska, P.J. Kulesza, Electroanalysis, 21 (2009) 351.

[2] B. Kowalewska, M. Skunik, K. Karnicka, K. Miecznikowski, M. Chojak, G. Ginalska, A. Belcarz, P.J. Kulesza, Electrochim. Acta 53 (2008) 2404.

10:00 Short communication

Hierarchical carbon nanotubes composite electrode – towards efficient enzymatic biocathodes based on direct electron transfer

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In the last four years, the proposed hierarchical carbon nanotubes (hCNT) composite material [1] grown onto ordinary graphite rod electrode demonstrated remarkable properties for supporting extensive loading with biological components and still facilitating excellent properties for efficient direct electron transfer (DET). In addition, this material shows high conductivity within the entire CNT network, as well as free access for the enzyme substrate towards the site with catalytic activity. In fact, the bioelectrochemical investigations of several redox enzymes was suggesting that the current density is dependent on the actual penetration length (or life span) of the substrate within CNT network.

Apart from the recently published example of HRP/hCNT biocathode [2], several other examples of enzymatic biocathodes constructed based on this hCNT material were investigated, such as: i) the co-immobilization of HRP/GOx for providing the first biocathode operating at +600 mV vs Ag/AgCl and relying on components compatible with physiological conditions and on *in-vivo* available substrates (glucose and oxygen); ii) the promoted adsorption of laccase using specific pyrene derivatives (see Figure 1); or iii) covalent linkage of bilirubin oxidase via its crosslinking with glutaraldehyde to the activated surface of the electrode.

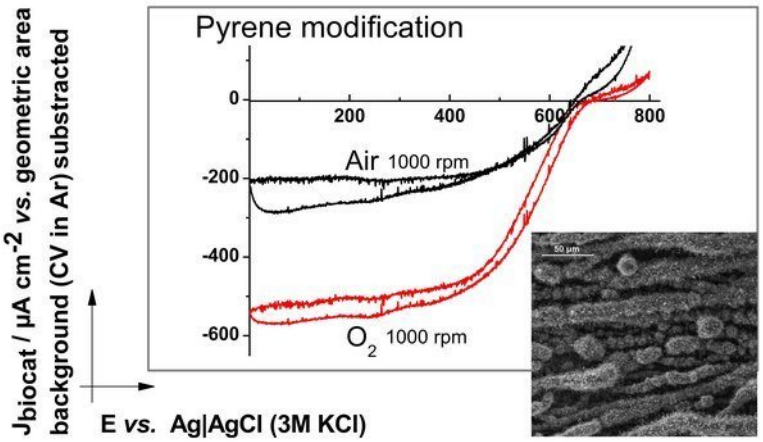

Figure 1. Cyclic voltammograme showing bioelectrocatalytic currents recorded at hCNT modified with a pyrene derivative and laccase. Insert- SEM image of hCNT composite material grown onto graphite rod.

The above examples and potential perspectives for further exploitation of this material will be presented.

[1] [1] Wenzhi Jia, Stefanie Schwamborn, Chen Jin, Wei Xia, Martin Muhler, Wolfgang Schuhmann and Leonard Stoica, Phys. Chem. Chem. Phys. (2010), 12(34)

[2] Nan Li, Xingxing Chen, Leonard Stoica, Wei Xia, Jun Qian, Jens Aßmann, Wolfgang Schuhmann, Martin Muhler, Advanced Materials (2007) 19 (19) 2957

10:15 Short communication

One-step electrodeposition of carbon–silicate sponge assisted by a three-phase junction for efficient bioelectrocatalysis

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Single-step electrodeposition of nanocomposite silicate materials based on hydrophilic carbon nanoparticles (CNPs) and a hydrophobic sol-gel precursor with the help of an electrode|organic-phase|aqueous-electrolyte three-phase junction is presented. A tin-doped indium oxide electrode is immersed into a cell filled with two immiscible liquids. The upper aqueous phase contains dispersed carbon nanoparticles in electrolyte and the bottom organic phase consists

of sol-gel precursor in nitrobenzene. Applying a positive potential to the electrode results in generation of protons which act as catalyst for the sol-gel process [1,2]. This method leads to the formation of a narrow, sponge-like carbon–silicate stripe at the electrode surface close to the three-phase junction. To increase the active surface area several parallel stripes were deposited, however this resulted in the formation of a compact film between the stripes. The morphology and structure of the nanocomposites were thoroughly investigated by AFM, SEM, optical and infrared mapping. The electrodes were examined as a support for bilirubin oxidase — an enzyme showing bioelectrocatalytic activity towards dioxygen reduction.

[1] M.M. Collinson, Acc. Chem. Res. 40 (2007) 777-783.
[2] J. Niedziolka, M. Opallo, Electrochem. Commun. 10 (2008) 1445-1447.

Coffee break

Sunday morning, 6 November, 10:30

Morning Session 2

Sunday morning, 6 November, 11:00
Chair: Shleev and Kulesza

11:00 Tutorial lectore

Recent developments in enzymatic biofuel cells

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Recent progress in miniaturized biofuel cells will be briefly reviewed with special focus on electrode surfaces nanostructured with carbonaceous nanomaterials and electron transfer without mediators [1-7]. Laccase binding to electrodes by means of arylated carbon nanotubes will be discussed and catalytic efficiencies of the chosen nanostructured electrodes will be compared. I will describe the preparation of the enzyme/SWCNT bioconjugates, and their application for the modification of the biocathode and bioanode. We test the catalytically active electrodes in the hybrid biofuel cell with Zn anode and if found useful - in the fully enzymatic biofuel cell. Carbon nanotubes functionalized with ethylamine group, activated and reacted with laccase were found promising for the biofuel cell applications. The power density of the hybrid biofuel cell based on the carbon nanotubes bound covalently to laccase on the cathode and Zn covered with Nafion layer as the anode reached 1 mW cm^{-2} at working voltage 0.8 V. The open circuit voltage of this hybrid cell was 1.5 V.

1. O. Yehezkeli, R. Tel-Vered, S. Raichlin, I. Willner, ACS Nano 5(2011)2385.

2. F. Gao, L. Viry, M.Maugey, P.Poulin, N. Mano, Nature Commun. 1/2 (2010)1.

3. K. Sadowska, K. Stolarczyk, J.F. Biernat, K.P. Roberts, J. Rogalski, R. Bilewicz, Bioelectrochem. 80 (2010) 73.

4. T. Miyake, S. Yoshino, T. Yamada, K. Hata, M. Nishizawa, J. Am. Chem. Soc., 133(2011)5129.

5. *R.P. Ramasamy*, H.R. Luckarift, D.M. Ivnitski, P.B Atanassov, G.R. Johnson, Chem. Commun. 46 (2010) 6045.

6. A. Zebda, C. Gondran, A. Le Goff, M. Holzinger, P. Cinquin, S. Cosnier, Nature Commun. 2 (2011)1.

7. A. Zloczewska, M. Jonsson-Niedziolka, J. Rogalski, M. Opallo, Electrochim Acta 56(2011)3947.

11:40 Keynote lecture

Enhancing heterogeneous electron transfer between enzymes and electrodes

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Enhancing heterogeneous electron transfer between enzymes and electrodes

Bioelectrocatalytic systems improve not only our knowledge about biocatalysts but also enable us to develop biomolecular moduls for bioanalytics, energy conversion and signal transfer. For effective bioelectrocatalysis it is essential to achieve a fast communication between the redox protein and the electrode, while the biocatalytic activity is preserved. Here we benefit from achievements in enzyme technology and surface science as well as from the progress made in the fabrication of support materials that serve as the interface between the biomolecules and the electrical circuit including the readout device. We will discuss recent approaches in this area. Examples are modified electrodes for measurement of aldehydes and sulfite using novel molybdoenzymes, which rely on mediated and direct electronic communication, nanoparticle facilitated electron transfer, and 3-D spectroelectrochemical devices with transparent conductive mesoporous electrodes.

12:00 Keynote lecture

Arranging proteins in electro-active multilayer architectures

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Electron transfer processes between proteins or within complexes of biomolecules represent an important type of biochemical reactions and signal transfer. The temporary or permanent assembly of proteins within complexes guarantees the accessibility of reaction sites, short electron transfer distances and minimal interference by other species. Artificial assemblies with a defined signal transfer which mimic the biological example may have application potential in sensors but also in biofuel cell systems. One important issue is here the coupling of the biochemical reactions to the electrode surface. For several redox proteins electrode surfaces have been optimized in order to achieve efficient heterogeneous electron transfer, such as heme, iron-sulfur and copper proteins [1-4].

Significant progress has been made in comparison to monolayer arrangements by use of the layer-by-layer-technique and the layered deposition of proteins on electrodes. Although the amount of protein can be significantly increased only the layers near to the surface are often able to exchange electrons directly with the electrode.

The presentation will give an overview on different approaches for the construction of fully electro-active protein multilayers. The assembly is based on the layer-by-layer deposition of the redox protein cytochrome c and a negatively charged second building block on electrodes, which can be the polyelectrolyte sulfonated polyanilline, carboxy-terminated gold or silica nanoparticles or a natural polymer dsDNA[5-8]. The unique property of these systems is the defined increase of electro-active protein amount with the number of deposited layers. The increase in electro-active amount can be advantageously used also for the detection of superoxide radicals with enhanced sensitivity[6]. The different building blocks however will influence the properties of the system. The succesfull assembly process is a first precondition for a functioning system and has been analysed by SPR or QCM, showing different behavior for dsDNA based systems compared to the particles and polyelectrolyte based assemblies.

From the mechanistic point of view it is obvious that not only a single system can be used for the construction of electro-active protein multilayers, however the question remains how the electrons are transferred through the layered system towards the electrode. Different arguments have been collected in different studies that electron exchange

between neighboring cyt c molecules might be the dominating mechanism[9-11]. However, mainly building blocks have been used which posses conducting properties by themselfs under certain circumstances. Recently silica nanoparticles have been prepared, modified with carboxylic groups and applied as building blocks for such protein assemblies. Since also here efficient electron transfer through several protein layers has been found, the model of a electron hopping between the immobilized cyt c molecules can be strongly supported. However, a flexibility at least on the rotational level, seems to be essential for the functioning of the system since covalent crosslinking of the cyt c molecules results in a loss of electroactivity.

These layered assemblies of a redox protein can be combined with enzymes in order to establish signal chains with multiple step electron transfer reactions following natural examples. Thus sensing electrodes for the enzyme substrate can be constructed. Signal transfer can be achieved by an internally generated shuttle molecule as shown for xanthin oxidase – cyt c layers[12] or more advantageously by direct protein-protein electron transfer without the need of any internal or external shuttle molecule. This can be shown for billirubin oxidase (BOD), laccase, sulfite oxidase and more recently cellobiose dehydrogenase (CDH) [13-16].

For example BOD can be co-immobilised with cyt c in multiple layers by means of a polyelectrolyte. The enzyme is catalytically active for oxygen reduction. The interesting properties are here that both reaction partners are immobilized on the electrode and that the catalytic oxygen current is increasing with the number of deposited layers. This means that BOD molecules immobilized in the outer layers still can communicate with the electrode by electron transfer from neighboring cyt c molecules. It has to be mentioned here that a rather high excess of cyt c has to be used during the assembly in order to connect the BOD molecules and transfer the electrons through the structure; higher amounts of enzyme disrupt the electron transport pathways [13]. Studies with mutant forms of cyt c demonstrate that a smaller self exchange rate lower the efficiency of electron transport through the system. However, besides the self exchange also the assembly properties and the reaction rate with the enzyme are determining factors[14].

The electron transfer can also occur in opposite direction as shown for assemblies with embedded CDH. Here electrons delivered by the oxidation of cellobiose or lactose have to be transported towards the electrode. Investigations of this bi-protein system also show that the interprotein electron transfer can be improved when the enzyme is used in a deglycosylated form. Much higher catalytic currents have been found.

References

1. M. J. Eddowes and H. A. O. Hill, *Journal of the Chemical Society-Chemical Communications,* 771-772 (1977)
2. S. Song, R. A. Clark, E. F. Bowden and M. J. Tarlov, *Journal of Physical Chemistry,***97**, 6564-6572 (1993).
3. K. A. Vincent and F. A. Armstrong, *Inorganic Chemistry* (2005) **44**, 798-809.
4. O. Ikeda, M. Ohtani, T. Yamaguchi and A. Komura, *Electrochimica Acta,***43**, 833-839 (1998).
5. M. K. Beissenhirtz, F. W. Scheller, W. F. M. Stocklein, D. G. Kurth, H. Möhwald and F. Lisdat, *Angewandte Chemie,***43**, 4357-4360 (2004).
6. M. K. Beissenhirtz, F. W. Scheller and F. Lisdat, *Analytical Chemistry,***76**, 4665-4671 (2004).
7. S. Bonk, F. Lisdat, *Biosensors and Bioelectronics,***25** (4), 739-744 (2009).
8. D. Sarauli, J. Tanne, D. Schäfer, I. W. Schubart, F. Lisdat, *Electrochemistry Communications,***11** (12), 2288-2291 (2009).
9. J. Grochol, R. Dronov, F. Lisdat, P. Hildebrandt and D. H. Murgida, *Langmuir,***23**, 11289-11294 (2007).
10. R. Dronov, D. G. Kurth, H. Möhwald, F. Scheller, J. Friedmann, D. Pum, U. B. Sleytr and F. Lisdat, *Langmuir,***24** (16), 8779-8784 (2008).
11. F. Lisdat, R. Dronov, H. Möhwald, F.W. Scheller, D.G. Kurth, *Chemical Communications,***3,** 274-283 (2009).
12. R. Dronov, D. G. Kurth, H. Möhwald, F. W. Scheller and F. Lisdat, *Electrochimica Acta,***53**, 1107-1113 (2007).
13. R. Dronov, D. G. Kurth, H. Möhwald, F. Scheller and F. Lisdat, *Angewandte Chemie,***47**, 3000-3003 (2008).
14. F. Wegerich, P. Turano, M. Allegrozzi, H. Möhwald, F. Lisdat, *Langmuir,***27** (7), 4202-4211 (2011).
15. T. Balkenhohl, S. Adelt, R. Dronov and F. Lisdat, *Electrochemistry Communications* (2008) **10**, 914-917.
16. R. Dronov, D. G. Kurth, H. Möhwald, R. Spricigo, S. Leimkuehler, U. Wollenberger, K. V. Rajagopalan, F. W. Scheller and F. Lisdat, *Journal of the American Chemical Society*, **130**, 1122 (2008).

12:20 Short communication

Gold nanoparticle-modified enzyme-based sugar and oxygen sensitive electrodes for biosensing and biofuel cell applications

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We report on the fabrication and characterisation of mediator-less sugar and oxygen sensitive biodevices based on three-dimensonal gold nanoparticle-modified electrodes with immobilised sugar oxidising and oxygen reducing enzymes. To create sugar and oxygen sensitive biodevices, *Corynascus thermophilus* cellobiose dehydrogenase (*Ct*CDH) and *Myrothecium verrucaria* bilirubin oxidase (*Mv*BOx) were used, respectively. For *Ct*CDH modified bioelectrodes maximal current densities of 28 μA cm^{-2} and 40 μA cm^{-2} could be obtained in the presence of 120 mM glucose and 5 mM lactose, respectively. It was shown that bioelectrocatalytic oxidation of sugars on *Ct*CDH-based electrodes was limited by the activity of the enzyme. Contrary, in the case of *Mv*BOx modified biodevices, a maximal current density equal to 110 μA cm^{-2} was obtained in air saturated solution due to mass transfer limitation.

By connecting the electrodes together a membrane- and mediator-less sugar/oxygen biofuel cell (BFC) was created operating in buffers and human physiological liquids. The following characteristics of the mediator-, separator- and membrane-less, miniature BFC, were obtained: open-circuit voltages of 0.68 and 0.65 V, maximum power densities of 15 mW cm^{-2} and 3 mW cm^{-2} at 0.52 V and 0.45 V of cell voltage, in phosphate buffer and human blood, respectively. The estimated half-lifes of biodevices were measured to be 24 h and 8 h in sugar-containing buffers and human physiological liquids, respectively. Thus, a mediatorless sugar/oxygen BFC with significantly improved basic characteristics compared to previously designed biodevices[1,2] could be constructed because of the usage of three-dimensional gold nanoparticle-modified electrodes.

1. V. Coman, R. Ludwig, W. Harreither, D. Haltrich, L. Gorton, T. Ruzgas, and S. Shleev. (2010) A direct electron transfer-based glucose/oxygen biofuel cell operating in human serum. Fuel Cells. 10(1), 9-16.2. V. Coman, C. Vaz-Domínguez, R. Ludwig, W. Harreither, D. Haltrich, A. L. De Lacey, T. Ruzgas, L. Gorton and S. Shleev. (2008) A membrane-, mediator-, cofactor-less glucose/oxygen biofuel cell. Phys. Chem. Chem. Phys. 10(40), 6093–6096.

Acknowledgements: The authors thank Amano Enzyme Inc. for Amano 3 preparation of *M. verrucaria* bilirubin oxidase. The authors would like to also thank Petri Gudmundsson and Karin Nilsson (Malmö University, Sweden) for their kind help with blood collection. Ms. Wang would like to thank the Finnish Graduate School of Chemical Engineering (GSCE) for the financial support to her PhD study and the scholarship for her research visit at Lund University in 2010. The work has been supported financially by the European Commission (FP7 project NMP4-SL-2009-229255) and the Swedish Research Council (projects 2007-4124, 2009-3266 and 2010-5031).

12:35 Short communication

The comparison of immobilization for glucose oxidase and horseradish peroxidase on titania nanotube surface

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A growing interest in using biosensors as a modern tool in the diagnosis and treatment of various diseases has been observed. Due to the use of an increasing number of detection techniques and design concept of biosensors, the range of materials used to construct sensors is expanding.

Titania nanotubes (TNT) are being investigated and developed intensively due to their advantageous qualities ie. good electrical properties, high surface area, excellent biocompatibility and controllable shaping.

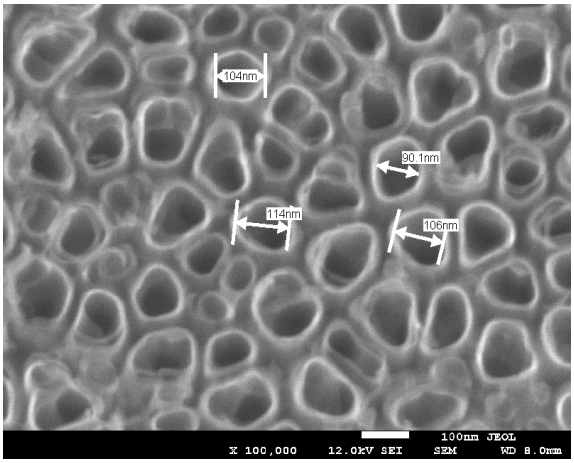

Figure 1. Surface morphology of anodic titania nanotubes formed on titanium in 1 M H_3PO_4 with 0.3% wt. HF

Significant changes in the flow of current after binding the biomolecules to nanotubes are caused by the direct proximity of the surface. The load and the conformation changing the molecule binding to these structures gives a large effect. This is why the selection of biomarker and the method of its immobilization is so important.

These studies compared the effect of immobilization method (dip or drop coating) and the influence of the immobilization time (24h and 48h) on the biosensor response in case of two model enzymes : the glucose oxidase (GOx) and horseradish peroxide (HRP) used to detect glucose or hydrogen peroxide (H_2O_2) in the PBS solution. The biological components covering the surface of the electrodes generate electrochemical response, making them the efficient and sensitive biosensors.

Firstly, using a matrix built of TiO_2 nanotubes (TNT) covered with enzymes as the platforms of the 3rd generation biosensor was assumed. The layer of TiO_2 nanotubes on titanium surface was obtained by anodization method and characterized using scanning microscopy. The material was annealed in a vacuum at 450ºC, and then glucose oxidase enzyme or horseradish peroxide were immobilized on its surface. The biosensor substrate was immersed in the enzyme solution for 24 and 48 hours. To check the biosensor response and to detect the presence of glucose or hydrogen peroxide in the PBS solution the cyclic voltammetry (CV) was used. In both cases the results were not satisfactory and the use of mediators was necessary. After using potassium ferricyanide as a mediator, an electric signal responsible for the process of catalytic oxidation of glucose was obtained. The analogous studies with the use of horseradish peroxidase enzyme and thionine acetate as a mediator were carried out giving the evidence of electrical response due to H_2O_2 presence in the PBS solution.TNT platform for the 3rd generation biosensor was considered.

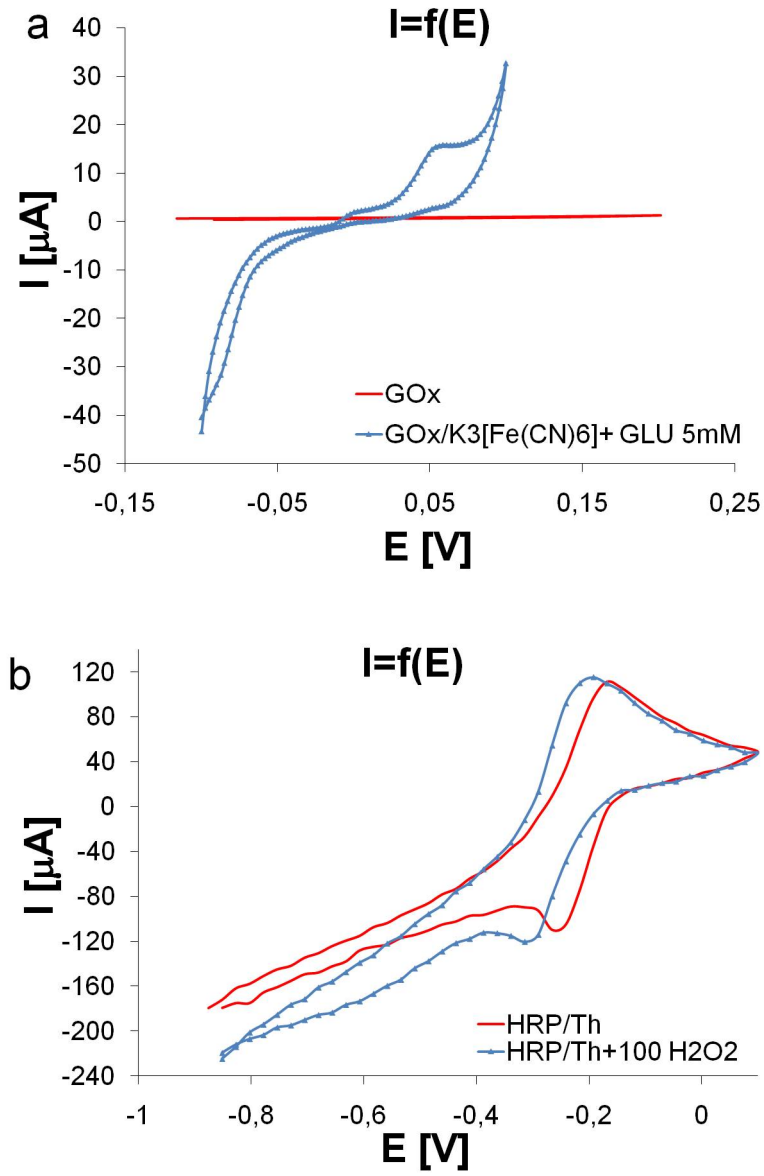

Figure 2. Cyclic voltamperometry measurements of : a) glucose biosensor – glucose oxidase GOx in PBS (pH 7.4), 0.1 M KCl and 5mM glucose, b) hydrogen peroxide biosensor - horseradish peroxidase HRP in PBS (pH 7.4), 0.1 M KCl and 100ml 30% H_2O_2

The studies allowed to elaborate the method of electrodes preparation of the 2nd generation biosensors based on titania nanotubes and will allow to optimize their structure as the efficient and simple biosensors.

Lunch break
Sunday afternoon, 6 November, 13:00

Afternoon Session 1

Sunday afternoon, 6 November, 14:00
Chair: Blanchard and Etienne

14:00 Tutorial lectore

Direct (mediator free) bioelectrocatalysis

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Bioelectrocatalysis is a phenomenon of acceleration of electrode reactions by the enzymes. Direct bioelectrocatalysis presumes the direct electron exchange between the enzyme active site and the electrode without any use of diffusion free mediators.

Direct bioelectrocatalysis is a discovery of Russian enzymologists and electrochemists. The discovery of the phenomenon in late 70-s realized in elaboration of oxygen enzyme electrode based on laccase. Later several other enzymes were involved in direct bioelectrocatalysis. The achievement of the substrate equilibrium potential was first shown with hydrogen enzyme electrode.

The history of direct bioelectrocatalysis, starting form electrochemistry of redox enzymes will be presented. The most successful examples for the enzymes in direct bioelectrocatalysis (including information on the structure of the enzymes) will be outlined. The approaches, how to involve enzymes in direct bioelectrocatalysis and the fundamentals of this phenomenon will be discussed.

Special attention will be paid to describe the novel approach: enzyme orientation during immobilization to improve efficiency of bioelectrocatalysis. The example of achievement of limiting performance characteristics of the enzymes in bioelectrocatalysis will be shown.

A rather novel phenomenon, the direct bioelectrocatalysis by intact cells, will be presented. An evidence for electroactivity of intact cells will be outlined, and the pictures, how bacteria are using electrode as an electron acceptor will be shown.

14:40 Keynote lecture

Direct electron transfer for myoglobin detection in human blood plasma and diagnosis of acute myocardial infarction

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Myoglobin (Mb) participates in human respiration both as an oxygen store and as an entity facilitating oxygen diffusion, thereby supporting cellular respiration in cardiac and skeletal muscle tissues. In addition to conventional functions, it can possibly act, as has been recently proposed, as an intracellular scavenger of nitric oxide (NO) to protect mitochondrial cytochrome *c* oxidase from its inhibition by NO.[1] In healthy organism, in the absence of inflammation or injury of muscle tissues myoglonin does not release into the circulation. Myoglobin detection is very important for express diagnosis of AMI, crush syndrome, hypoxia neonatorum, overtraining of sportsman, as well as in forensic medicine as an additional criterion for fatal poisoning with ethanol and drugs of opiate group.

Myoglobin belongs to the family of heme proteins, whose active center (heme) contains a coordinated Fe(III) ion. Our research group was the first to make use of the electrochemical properties of myoglobin for its detection in biological body fluids.[2-4] The proposed method is based on internal electroactivity of myoglobin and direct detection of its interaction with specific antibodies. Thus, myoglobin can be quantitatively detected by direct electron transfer reaction from an electrode surface to ion Fe(III):

$$\text{Mb–Fe(III)} + e^- + H^+ \rightarrow \text{Mb–Fe(II)};$$

$$\text{Mb–Fe(II)} + O_2 \rightarrow [\text{Mb–Fe(II)}O_2] \rightarrow \text{Mb–Fe(III)} + O_2^-$$

In this scheme, oxygen participates in the catalytic reaction. However, this electrocatalytic reaction may be realized only by using special modifiers of the electrode surface, its nanostructuring. Nanostructuring provides direct electron transfer between electrode and the myoglobin heme, thus enabling to register the signal and to reach a very low limit of detection. Golden, silver, copper nanoparticles and carbon black were used for electrode surface modification. It was shown that carbon black dispersion improves the sensitivity of myoglobin detection.

Cathodic peak of cardiac Mb reduction was proportional to Mb concentration in human plasma. The required sample volume is 0.25–1 μl depending on the electrode surface, while the analytical procedure takes no more than 30 min. The developed electrochemical method can be used for express diagnostics of acute myocardial infarction, other diseases and disease states, as well as, for investigation of myoglobin functions in physiological processes.

This work was financially supported by the Federal Agency of Science and Innovations, Russian Federation Ministry of Education and Science (Contract № 16.512.11.2215).

1. K. Shikama, *Progress in Biophysics and Molecular Biology* 2006, 91, 83;

2. V. Shumyantseva, E. Suprun, T. Bulko, A. Archakov, *Electroanalysis* 2009, 21, 530;

3. E. Suprun, T. Bulko, A. Lisitsa, O. Gnedenko, A. Ivanov, V. Shumyantseva, A. Archakov, *Biosens. Bioelectron.* 2010, 25, 1694;

4. E. V. Suprun, A. L. Shilovskaya, A. V. Lisitsa, T. V. Bulko, V. V. Shumyantseva, A. I. Archakov, *Electroanalysis* 2011, 23, 1051;

15:00 Short communication

Size and Zeta Potential of Lipid Vesicles with Incorporated Calixarenes at Presence of Cytochrome c and PAMAM Dendrimers

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Calix[n]arenes (CX) are macrocyclic aromatic molecules, which originate from the coupling of phenols and aldehydes. The index [n] refers to the number of phenol aromatic cycles in the molecule. In a calixarene molecule, phenol subunits are bridged via methyl groups. This provides the characteristic vase-like shape of the CX molecule. Moreover, modification of the side groups of CX allows one to prepare tailor-made receptors with high affinity for specific target molecules1. Recently CX (n=6) sensitive to cytochrome c (cyt c) has been demonstrated2. Cyt c is small hemoprotein (M.w. 12.4 kDa) found in the intermembrane space of mitochondria. Under physiological conditions it is positively charged owing to lysine and arginine amino acid residues. Cyt c plays a dual role in living system. It participates in electron transport and is responsible for the activation of the apoptotic pathway through releasing from mitochondria into the cytosol. CX can be incorporated into the lipid films and this system may be useful for detection cyt c. The biosensor based on CX incorporated into the supported lipid membranes has been reported3. However, mechanism of cyt c interaction with CX is not yet known. G4 PAMAM (M.w. 14.1 kDa) has similar size like cyt c and is also positively charged. Therefore G4 can serve as a model of non-specific interactions. At the same time G4 is useful for drug delivery. Therefore analysis of G4 interaction with model membranes containing receptors

is of high importance. We studied the interaction of cyt c and G4 PAMAM with CX incorporated into the large unilamellar vesicles (LUV, diameter 100 nm) composed of dimyristoylphosphatidylcholine (DMPC). We showed that with increasing concentration of CX the average size of LUV increased and zeta potential become more negative as it is suggested from dynamic light scattering experiments. Cyt c did not affect significantly the LUV size, bur reduced the negative zeta potential of CX containing vesicles. Similarly to cyt c G4 also reduced negative charge of CX containing LUV. G4 did not affect the size of unmodified LUV, however at c> 1 mM the average diameter of vesicles modified by CX substantially increased from 100 to approx. 500 nm which suggest vesicle aggregation. It is likely that main driving force of interaction cyt c and G4 with CX containing vesicles is negative charge of CX carboxyl groups.

Acknowlegements: This work was supported by Slovak Research and Development Agency (Contracts No. APVV-0410-10, LPP-0250-09 and SK-PL-0034-09) and Grant Agency VEGA (Project No.1/0794/10).

1. Gutsche, C. D., Muthukrishnan, R. J. Org. Chem. 43 (1978), 4905-4906

2. Oshima, T., Ishii, T., Baba, Y., Higuchi, H., Ohto, K., Inoue, K. Solv. Extr. Res. Dev. Japan 15 (2008), 89-98

3. Mohsin, M.A., Banica, F-G., Oshima, T., Hianik, T. Electroanalysis 23 (2011) 1229 – 1235

15:15 Short communication

One-step reduction and functionalization of graphene oxide sheets using biomimetic dopamine derivatives

Izabela Kamińska[1,2], Manash Das[3], Joanna Niedziolka-Jonsson[1], Patrice Woisel[4], Joel Lyskawa[4], Marcin Opallo[1], Rabah Boukherroub[2], Sabine Szunerits[2]

1. *Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, Warszawa 01-224, Poland* **2.** *Institut de Recherche interdisciplinaire (IRI), 50 avenue de Halley, BP 70478, Villeneuve d'Ascq 59652, France* **3.** *North East Institute of Science and Technology (NEIST), Assam 785006, India* **4.** *Unite des Materiaux Et Transformations, Equipe Ingenierie des Systemes Polymeres (UMET-ISP), Villeneuve d'Ascq 59658, France*

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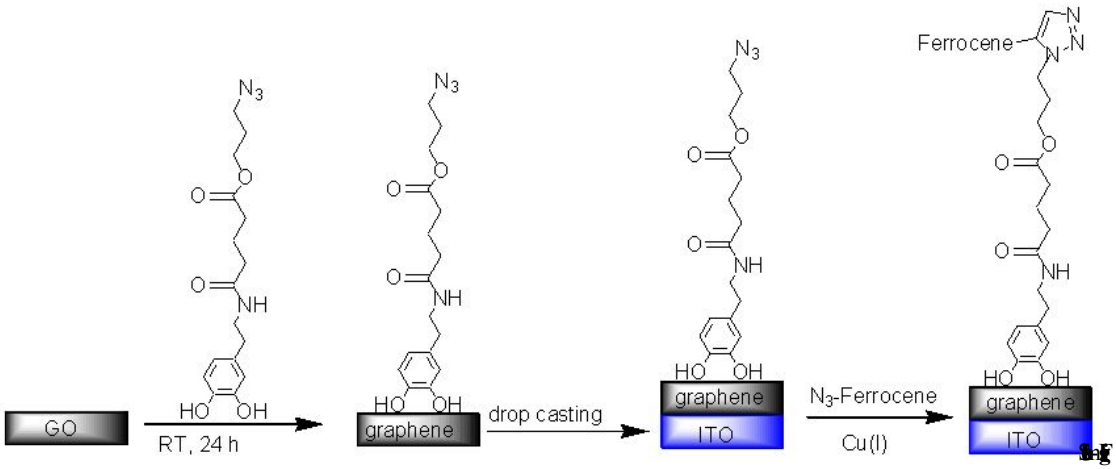
Graphene has attracted a great deal of scientific and technological attention in recent years due to its unique electronic, mechanical and thermal properties [1-3]. A great promise has been shown for applications in different areas such as electronics, energy storage and conversion as well as in the development of biosensors [4-7].

Here, we demonstrate that graphene oxide can be reduced to graphene by adding azide-terminated dopamine. The reduced character of graphene was investigated using cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS). Next, "click" reaction has been performed using graphene modified with azide-terminated dopamine and alkyne-terminated ferrocene. The interaction between dopamine and graphene is based on π-stacking interactions between the hexagonal cells of graphene and the aromatic ring structure of dopamine [8]. The success of the "click" reaction was confirmed by XPS and CV as well as FTIR.



atic illustration of the preparation of azido-dopamine capped grahene nanosheets.

References

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science*, **306**, 666 (2004).

2. M. J. Allen, V. C. Tung, and R. B. Kaner, *Chem. Rev.*, **110**, 132 (2009).

3. Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, and Y. Lin, *Electroanalysis*, **22**, 1027 (2010).

4. L. X. Li, G. Y. Zhang, X. D. Bai, X. M. Sun, X. R. Wang, E. Wang, and H. J. Dai, *Science*, **319**, 1229 (2008).

5. F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, *Nat. Mater.*, **6**, 652 (2007).

6 . H.-X. Wang, K.-G. Zhou, Y.-L. Xie, J. Zeng, N.-N. Chai, J. Li, and H.-L. Zhang, *Chem. Commun.*, **47**, 5747 (2011).

7. S.-Y. Yang, K.-H. Chang, H.-W. Tien, Y.-F. Lee, S.-M. Li, Y.-S. Wang, J.-Y. Wang, C.-C. M. Ma, and C.-C. Hu, *J. Mater. Chem.*, **21**, 2374 (2011).

8. L. Q. Xu, W. J. Yang, K.-G. Neoh, E.-T. Kang, and G. D. Fu, *Macromolecules*, **43**, 8336 (2010).

COFFEE

Sunday afternoon, 6 November, 15:35

Afternoon Session 2

Sunday afternoon, 6 November, 16:00

Chair: Karyakin and Lisdat

16:00 Tutorial lectore

Organization and Dynamics within Supported Interfaces: Implications for the Creation of Biomimetic Structures

Stephan Baumler, Benjamin P. Oberts, Monika J. Dominska, Gary J. Blanchard

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The creation of biomimetic support structures capable of supporting transmembrane proteins in their active form has proven to be a challenging task. The inherent structural and compositional complexity of the plasma membrane makes the task of creating a synthetic equivalent difficult. Issues such as the composition and morphology of supporting underlayers and the attachment of a biomimetic layer to an interface are central to success. Much of the recent focus of our group has been on methods for binding lipid adlayers to interfaces while retaining fluidity. A substantial concern for such systems is the extent to which the interfacial structure is influenced by the interface binding chemistry and its immediate environment. An overview of recent advances in this area will be presented.

16:40 Tutorial lectore

Micro and nanofabrication of molecularly imprinted polymer synthetic receptors for sensing applications

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Molecularly imprinted polymers (MIPs) are synthetic receptors produced by molding a polymer around a molecular template. MIPs may be used in the place of biomolecules as recognition elements in various applications including chemical sensors and biochips.

One of the main challenges in this respect is the interfacing of the MIP with a transducer. This is particularly true when micro or nanopatterns of MIP are to be generated, for example for multisensors or integrated microbiochips.

This talk will present different possibilities of patterning MIPs at surfaces, using techniques like micro and nanofountain pen deposition, contact and projection photolithography, soft lithography, nanomoulding, and controlled polymerisation. In addition, a number of different optical method to specifically detect the presence of the target molecule in the MIP will be described, in particular by surface-enhanced Raman spectroscopy. A few examples of microsensors, microbiochips, and individual nanosensors based on MIPs will be discussed.

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17:20 Short communication

Advantages and frontiers of Molecularly Imprinted Polymers – from fundamentals to application

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In recent years, solid phase microextraction (SPME) has been applied widely to the analysis of environmental, food, biological and pharmaceutical samples. Compared with the conventional extraction techniques SPME is simple, sensitive, time efficient, solvent-free, and compatible with the analytical separation systems such as gas chromatography (GC), GC – mass spectrometry or high-performance liquid chromatography (HPLC). In present days new kind of sorbents are being developed and applied for achieving better sorption efficiency and higher selectivity. One of these kind of sorbents can be molecularly imprinted polymers (MIP'S).

Molecular imprinting is a technique to prepare molecular recognition materials. It has shown an accepted application prospect in many fields such as materials of solid-phase extraction, simulated enzyme catalysis, chemical sensors or membrane separations. MIP is quite suitable as a material of SPME fibre coating because of high selectivity, chemical stability and easy preparation.

In this research molecularly imprinted polymer sorption material which can be later used for SPME improvement were prepared. In first step non-molecularly imprinted polymer was prepared. For this six different solvents such as acetonitrile, n-heksane, dimethylforamide,dichloromethane or chloroform were used. As functional monomer methacrylic acid (MAA) was used. Crosslinker agent was ethylene glycol dimethacrylate (EGDMA). As polymerization initiator azo(bis)-isobutyronitrile (AIBN), benzoil peroxide, hydrogen peroxide, ammonium sulfate peroxide and g-radiation were used. During the synthesis different sorbents were produced. Further the same syntheses used additionally as the template ibuprofen were done. In this step molecularly imprinted sorption material (MIP) was prepared. Thermal stability of all the samples was checked by thermal analysis. Pore sizes and BET surface were characterized by sorption of nitrogen. Also the homogeneity and structure of surface of prepared materials was examined using scanning electron microscopy.

17:35 Short communication

Molecularly imprinted polymer based electrochemical sensors for flow injection determination of adrenaline

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The electrochemical sensors were fabricated for selective and sensitive determination of adrenaline. In these sensors, a thin film of the adrenaline-templated molecularly imprinted polymer (MIP) was used for adrenaline recognition and differential pulse voltammetry (DPV) and piezoelectric microgravimetry (PM) for analytical signal transduction under flow-injection analysis conditions. First, molecular structure of a complex (Scheme 1) of protonated adrenaline (HAd) with the benzo-(18-crown-6) (Cr6BTP) and benzoic acid (COOHBTP) derivatives of bis(2,2'-bithienyl)methane, used as electroactive functional monomers, was optimized with the B3LYP/6-31g(d) density functional theory method by the Gaussian 03 software. Then, the MIP film was deposited on a Pt disk electrode and 10 MHz quartz crystal resonator (QCR) by potentiodynamic electropolymerization from a solution of HAd, Cr6BTP, CHOBTP, and the cross-linking tris(2,2'-bithienyl)methane monomer at the mole ratio of 1:1:1:2. Next, the adrenaline template

was extracted with 0.01 M NaOH from the MIP film; completeness of the extraction was confirmed by XPS. For adrenaline determination, the decrease of the DPV peak current for the 0.1 M $K_4[Fe(CN)_6]$ redox probe and the change of the resonance frequency of the 10 MHz QCR, proportional to the adrenaline concentration, was measured.

Gala Dinner
Sunday evening, 6 November, 18:00

Monday, 7 November

Breakfast
Monday morning, 7 November, 8:00

Excursion
Monday morning, 7 November, 9:00

Lunch break
Monday afternoon, 7 November, 13:00

Afternoon Session 1
Monday afternoon, 7 November, 14:00
Chair: Wadhawan and Nagels

14:00 Tutorial lectore

Microbial Fuel Cell: A fascinating technology and interdisciplinary challenge

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The globally growing energy demand and environmental issues like the green house effect require the development of clean and renewable energy sources. At the same time, increasing amounts of energy are consumed for the treatment of anthropogenic waste products like sewage. Microbial fuel cells (MFCs) produce electricity by utilising the metabolism of living microorganisms to catalyse the oxidation of organic or inorganic substrates for electricity production. By doing that they offer access to a direct generation of electricity from low-value biomass, such as agricultural wastes and sewage. This potential combination of waste treatment and power generation has recently led to a tremendously growing interest in microbial fuel cells and to substantial research progress.

The performance of a microbial fuel cell (MFC) depends on a complex system of parameters. Apart from operational variables like the anode or fuel cell design, it is mainly the paths and mechanisms of the bioelectrochemical energy conversion that decisively determine the MFC power and energy output. Here, the electron transfer from the microbial cell to the fuel cell anode, as a process that links microbiology and electrochemistry, represents a key factor that defines the theoretical limits of the energy conversion.
This lecture will provide an introduction into the principles of microbial bioelectrochemical fuel cells and related (microbial) bioelectrochemical systems. Recent approaches and developments will be discussed.

14:40 Keynote lecture

Chemically modified nanoparticles surface for sensing bacterial loading - experimental study based on fluorescent signal

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The bacterial loading of liquid media, either environmental or biological ones, could be detected through various methods, based on microorganism features as well as on the interactions developed with chemical or physical factors. Since in previous studies the magnetite nanoparticle ability of changing the intensity of the fluorescent signal released by *Pseudomonas aeruginosa* cells was revealed, the influence of magnetite nanoparticle surface on the green-bluish emission of bacterial cells was chosen as the target of the present investigation.

Magnetite nanoparticles were prepared by co-precipitation method being further stabilized in aqueous suspension by coating with organic shells. Two types of magnetite core stabilization were accomplished: electrostatic – based on iron ions interaction with tetramethyl ammonium hydroxide (TMA-OH) and steric – by means of sodium oleate coating. Average crystallite diameter was evaluated (by X-ray diffractometry) at 13.6 nm (for magnetite core/TMA-OH shell) and respectively 12.13 nm (for magnetite core/sodium oleate shell), while saturation magnetization was found of about 24 emu/g, and respectively, 49 emu/g.

The *P. aeruginosa* bacteria were proved to present increased fluorescent signal for magnetite suspension in the culture medium of the order of magnitude of microl/l, so that the surface modified magnetite particles could be taken as probes in the basic structure of a chemical sensor for bacterial loading detection. Our experiments consisted in the recording of fluorescent emission as well as of the turbidity of *P. aeruginosa* samples with cell density ranging from 10^8 cell/ml up to 10^2 cell/ml - the latest representing the level of the possible microbial contamination of injectable antibiotic drugs. The same range of inoculum cell density was spectrofluorimetrically investigated in the presence of coated magnetite suspension – the influence of the coating shell on the fluorescent signal being discussed. The sensitivity of the proposed chemical sensing system was discussed related to the slope of the fluorescent signal intensity versus inoculums density.

The molecular background of the interaction between the colloidal magnetite and the microbial cells is given by the biosynthesis of the fluorescent siderophore named pyoverdine –stimulated for low iron loading of the environment due to the bacteria behavior as iron scavenger. Though the cellular mechanisms of iron internalization could not be elucidated from the data acquired in the frame of this experimental study, however it was evidenced the possibility of designing of a chemical sensing device able to detect small contamination level with the fluorescent bacteria *P. aeruginosa* of antibiotic products, biological specimens and environmental samples. The chemically modification of the magnetite nanoparticle surface could provide the means of sensor sensitivity monitoring according to the contamination level of the tested bacterial samples.

15:00 Keynote lecture

Hybrid Sol-Gel Materials for Bioelectrochemical Applications

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The sol-gel process provides unique opportunity to produce hybrid materials combining simultaneously organic and inorganic properties in a single solid [1]. In addition, the porosity of such materials can be tuned and the shape of the solid can be adapted to the application, from monolith to particles and thin films. Sol-gel silica material also allows for the encapsulation of protein, bacteria and biological cells in an active form without preventing the diffusion of molecules (enzymatic substrate, nutriments, etc.) inside the porous gel network and provides a protective environment that allows a better resistance of the encapsulated biological object to harsh conditions (temperature, pH, etc.) and/or an improved long term stability [2].

This communication will show some examples of hybrid sol-gel thin films for bioelectrochemical applications. Indeed, we recently investigated the co-immobilization in a single film of a NAD-dependant dehydrogenase (D-sorbitol, D-Glucose or L-Lactate dehydrogenase), the NAD^+ cofactor and a suitable electrocatalytic system for allowing the safe detection-regeneration of the cofactor during the bioelectrocatalytic reactions [3-6].

We will see that such a complex layer can be successfully prepared with using the different possibilities offered by the sol-gel chemistry, i.e. the incorporation of polyelectrolytes, the co-condensation with chosen organoalkoxysilane and finally the processing for getting a thin film on the electrode surface. The method used to prepare the film, the evaporation of the starting sol (drop or spin-coating) or the electrochemically assisted deposition, affected strongly the bioelectrochemical response of the modified electrodes. These results will be discussed in a tentative to define the best strategy to be used according to the electrode to be modified (flat or porous electrodes) and the concerned application (biosensor, electroenzymatic synthesis, biobattery or biofuel cell).

[1] C. Sanchez ,L. Rozes, F. Ribot, C. Laberty-Robert, D. Grosso, C. Sassoye, C. Boissiere, L. Nicole, *C. R. Chimie***2010**, *13*, 3.
[2] D. Avnir, T. Coradin, O. Lev, J. Livage, *J. Mater. Chem.***2006**, *16*, 1013.
[3] Z. Wang, M. Etienne, G.-W. Kohring, A. Walcarius, *Electroanalysis***2010**, *22*, 2092.
[4] A. Walcarius, R. Nasraoui, Z. Wang, F. Qu, V. Urbanova, M. Etienne, A. S. Demir, J. Gajdzik, R. Hempelmann, *Bioelectrochem.***2011**, *82*, 46.
[5] Z. Wang, M. Etienne, G.-W. Kohring, Y. Bon-Saint-Côme, A. Kuhn, A. Walcarius, *Electrochim. acta*, in press.
[6] Z. Wang, M. Etienne, F. Quilès, G.-W. Kohring, A. Walcarius, *submitted*.

Coffee Break

Monday afternoon, 7 November, 15:35

Afternoon Session 2

Monday afternoon, 7 November, 16:00
Chair: Schröder and Gorton

16:00 Tutorial lectore

Fundamentals in lithium ion batteries: effect of surface modification on the bulk process

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Lithium-ion batteries are now used in a wide range of applications, particularly in connection with portable electronic devices. The wide interest and application range is due to the high power and energy density of such a system, as well as its life time. The challenge of using these systems in larger applications such as for personal or public transportation requires improvements in energy and power density, and also cycle life. This challenge cannot be achieved without a proper understanding of the surface phenomena that occur at the electrolyte/active material interface.

Although the intercalation reaction, which ensures the storage of energy in lithium-ion batteries, is a bulk process, it has been observed and demonstrated that surface modifications of the bare active materials can influence strongly the coulombic efficiency of the ion storage and the cycle life of the battery itself. Moreover, during the charge and discharge processes, the active materials in the battery, and also the conductive additives, are subjected to surface modification, triggered by the oxidation or reduction of the components contained in the organic electrolyte. The oxidation and reduction products, that form the solid electrolyte interphase (SEI) between the active material and the electrolyte, are studied by differential electrochemical mass spectrometry (DEMS) and electrochemical impedance spectroscopy (EIS).
An overview on the fundamentals of the intercalation/deintercalation process in lithium-ion batteries will be given, with particular focus on the modifications that occur on the surface of carbonaceous materials and lithium metal oxides, due to their interactions with the organic electrolyte (ethylene carbonate, dimethyl carbonate, diethyl carbonate, propylene carbonate). The effect of surface modification on the SEI and on the performance of the lithium-ion battery will be addressed.

16:40 Keynote lecture

Is it possible to study Interaction of molecules with sensor surfaces/components, using potentiometric "sensorgrams"?

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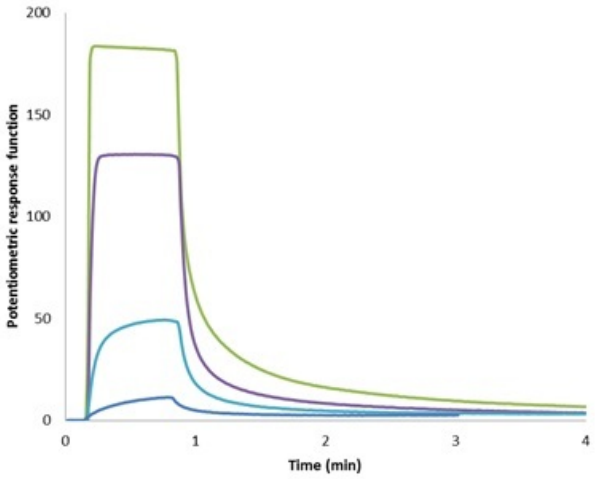
The present study explores the possibility to use the sensorgram methodology, which is very common in surface plasmon resonance (SPR), in potentiometry. Can we obtain information on rates of adsoption/ion exchange of ionized organic molecules from their response behavior on a potentiometric sensor? And do we see changes in this behavior if we add a (e.g. protein) biomolecule in the sensor coating? The answer is yes. Sensorgrams were obtained by injection of square concentration pulses in a flow injection (FIA) setup with a flow-through system. The compounds studied include metabolic acids, environmental contaminants, basic drugs plus alkaloids, and oligonucleotides. As potentiometric sensor coatings we compare a soft, hydrophilic gelatin based coating with a classical lipophilic rubber based coating. The substrate (contact layer) of these coated wire type sensors was a conductive composite. The "on" and "off" kinetics (k_{on} and k_{off}) were studied as a function of analyte characteristics, analyte concentration, contact time, hydrodynamics, sensing layer type, and addition of biomolecules to the sensing layer. The figure in this abstract shows sensorgrams for promazine on a classical rubber membrane injected at concentrations 10^{-7}, 10^{-6}, 10^{-5} and 10^{-4} M. It will be discussed in relation to analogous SPR sensorgrams. Adsorption on- and diffusion in the sensor's coating materials are shown to be active during the contact times which varied between 10 and 40s. Large flexible analyte molecules with high interaction with the surface (components) yield the slowest "on" (phase transfer) kinetics. In the soft gelatin material, diffusion becomes more predominant as compared to the hard rubber materials. This gelatin material can be easily doped with a (protein or DNA) biomolecule. This is very promising in view of future qualitative and quantitative use of potentiometric sensor response dynamics in analyte/biomolecule and analyte/surface studies. Compatibility of the sensors with separation methods is also briefly discussed.



17:00 Short communication

Liquid Crystal Battery Systems

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The development of new and efficient forms of energy storage is important for the current technological age. In this talk we will examine the use of lyotropic liquid crystals as frameworks for exploitation as multi-stacked battery systems. We will examine the interplay between diffusion and electron transfer at the crossphase interface, and examine the role played by reagent partitioning.

17:15 Short communication

Composites of electroactive fullerene-based polymer and carbon nanomaterials – good materials for supercapacitors

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Thin films of composites of electroactive fullerene-based polymer and carbon nanomaterials (carbon nanotubes and carbon nano-onions) were electrochemically prepared by electrodeposition of polymer on the layer of carbon nanoparticles immobilized at the electrode surface. Processes of composites formation were investigated by cyclic voltammetry, electrochemical impedance spectroscopy, piezoelectric microgravimetry and transmission electron microscopy.

The electrochemical properties of films depend on the carbon nanoparticles used for its formation and the film composition. Formed materials are electrochemically active in negative potential range due to the electroreduction of fullerene moieties. In this potential range, composites behaves as typical redox pseudo-capacitors. Much better capacitance properties were observed for films containing carbon nanotubes in comparison to composites of carbon nano-onions. A specific pseudo-capacitance up to 425 F g^{-1} was found for multiwall carbon nanotube/C_{60}-Pd composite.

The presence of carbon nanomaterials makes the composite conductive also at potentials less negative than potentials of C_{60} electroreduction. The double-layer specific capacitance of this film is close to 40 F g^{-1}.

17:30 Short communication

Redox Reactivity of Methylene Blue in the Pores of UMCM-1 Metal-Organic Frameworks

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Redox processes are studied in the molecular pores of a crystalline UMCM-1 metal organic framework (MOF) material. Methylene blue is employed as an absorbed redox active dye component. From the change in coloration during dye adsorption, it can be concluded that an essentially irreversible adsorption process with high pore loading of the resulting MOF structure occurs. The adsorbed methylene blue remains redox active in the MOF pores and there is no evidence of losses during extended redox cycling. Due to the size of the pores, the reactivity of the pore-bound methylene blue is closely related to that expected for methylene blue in aqueous solution. A study of the effect of solution pH on the voltammetric responses reveals an interesting gradual change in electrical pore conductivity form poorly conducting under acidic conditions to highly conducting under alkaline conditions and this is interpreted in terms of charge transport via single-electron hopping conduction in pores.

17:45 Short communication

Polymeric and nanostructured composites containing lignin derivatives

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The term *lignin* is used to describe both naturally occurring biopolymer binding cellulose fibers together in plant cells and a byproduct from paper/pulp industry which in fact is a variety of chemical derivatives of the former characterized by lower molecular weight, altered chemical structure and solubility in aqueous and/or organic phases. From chemical point of view, the parent lignin is an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, coumaryl, coniferyl and sinapyl alcohol [1]. Being polyphenolic compounds lignin derivatives show substantial electrochemical activity especially in the range of anodic potentials. This talk will focus on the electrochemical properties of two types of technical lignins i.e. kraft lignin and lignosulfonates obtained from sulfide pulping and sulfite pulping respectively. As it will be shown, the two materials as redox active biopolymers with some polyelectrolyte surfactant properties could be applied as:

- dopands of conducting polymers,
- constituents of oxide based nanocomposites based on ZnO and SiO_2,
- dispersing and stabilizing agents of carbon nanotubes [2],
- dispersing and stabilizing agents of metal nanoparticles e.g. silver or gold.

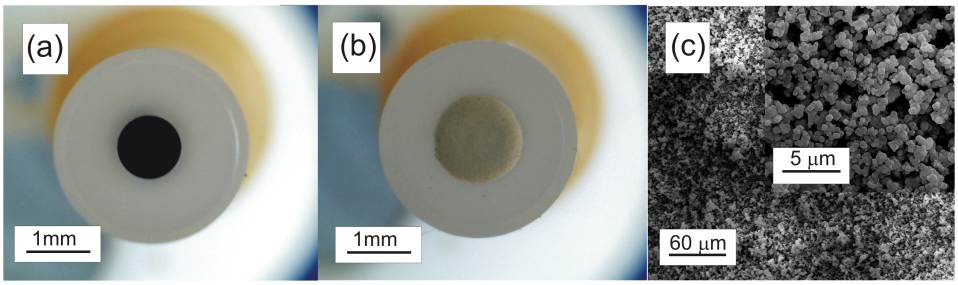

Fig. 1. Photographs of a glassy carbon electrode before (A) and after electrophoretic deposition of silica/lignin biocomposite (B). (C) – SEM pictures of electrophoretic silica/lignin deposit at two magnifications

Many examples of the application of such materials in electrochemical sensing will be presented and discussed.

Acknowledgement

This work was financially supported by Ministry of Science and Higher Education (Poland)under project No. N N209 450939.

References

[1] Donaldson, L. A. Phytochem. 2001, 57, 859.

[2] Milczarek, G., J. Electronal. Chem. 2010, 638, 178.

Dinner
Monday evening, 7 November, 18:00

Dance session
Monday evening, 7 November, 19:00

Tuesday, 8 November

Breakfast
Tuesday morning, 8 November, 8:00

Morning Session 1
Tuesday morning, 8 November, 9:00
Chair: Marken and Krysiński

9:00 Tutorial lectore

Electrochemical ion-sensors in clinical chemistry - challenges and perspectives

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Electrochemical sensors and associated electroanalytical methods are used on a massive scale in clinical analysis. It is owing to their attractive functional parameters and the possibility of their use in high throughput random access analyzer as well as in bed-side and point-of care disposable testing. In particular, potentiometric and amperometric measurements of pH, gases, electrolytes and glucose frequently employed [1]. Emphasis on the reliability of instruments, traceability of measurments, cost reduction of tests and running costs of the laboratory, and *last but not least*, automation increase the need for improvements and innovations which take place through the introduction of new materials and manufacturing technology of the sensors. This, in turn, introduces new research challenges, among which - alongside the traditional tasks such as improving the properties of electroactive components and electrodes – is the miniaturization of sensors (*nanosensors*), their integration (*all-solid-state*) and the need for direct measurement in short time, in a small sample volume and regime of low detection limits [2-4].

For signal interpretation and theoretical modeling, the present demands for new applications of ion-sensors actually mean that one should leave the current theoretical paradigm of potentiometry, which assumes equilibrium or stationary states. A new theoretical interpretation should be able to predict potentiometric signal in time and space. This can be done by resolving Nernst-Planck-Poisson (NPP) system of equations [5]. Furthermore, with the NPP it is possible to address the desired target function (e.g. linear calibration curve) via reverse modeling. The latter procedure can be used for the optimization of sensor properties e.g. to lower the detection limit of ion-selective electrodes or as a diagnostic tool [6].

In the lecture - on the example of measurement standards developed by the International Federation of Clinical Chemistry (IFCC) [1] – the role of world-wide valid recommendations is emphasized. In *a real life*, both new sensor designs and theoretical interpretations of the response are finally confronted with reasonably conservative regulations concerning the quality of measurements as accepted in medical diagnostic practice. This approach will allow to tune research enthusiasm of the speaker and to adjust the message for a realistic presentation of the prospects and challenges in the ion-sensor research field.

References

[1] A. Lewenstam, *Clinical analysis of blood gases and electrolytes by ion-sensitive sensors,* in: S. Alegret, A. Merkoci (eds.), *Electrochemical Sensor Analysis (Comprehensive Analytical Chemistry vol. 49)*, Chapter 1, Elsevier, Amsterdam 2007.

[2] J. Bobacka, A. Ivaska, A. Lewenstam, Chem. Rev., 108 (2008) 329.

[3] J. Migdalski, B. Baś, T. Błaż, J. Golimowski and A. Lewenstam, J. Solid State Electrochem., 13 (2009) 149.

[4] B. Paczosa-Bator, M. Stepień, M. Maj-Żurawska, A. Lewenstam, Magnesium Res., 22 (2009) 10.

[5] T. Sokalski, W. Kucza, M. Danielewski, A. Lewenstam, Anal. Chem., 81 (2009) 5016.

[6] B. Grysakowski, J.J. Jasielec, B. Wierzba, T. Sokalski, A. Lewenstam, M. Danielewski, J. Electroanal. Chem., (2011) doi:10.1016/j.jelechem.2011.04.026.

9:40 Keynote lecture

New affinity biosensors as diagnostic tools for biomedical analysis

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Over the last decade, great attention has been paid to the integration of newly developed nanomaterials such as nanowires, nanotubes and nanoparticles in biosensor systems. The reason can be traced to their technologically important combination of properties, such as high surface area, good electrical properties, chemical stability and ease of miniaturisation, which make them very promising for the realisation of nanoscale bio-electronic device.

Moreover, the field of molecular diagnostics has expanded rapidly. Applications range from the detection of mutations responsible for human inherited disorders, disease-causing and food-contaminating viruses and research into bacteria and forensics. Detection of infectious species and genetic mutations at the molecular level opens up the possibility of performing reliable diagnosis even before any symptom of a disease appears. Additionally, the development of novel therapeutics based on the regulation of gene expression provides revolutionary new opportunities in the area of pharmaceutical science.

Focusing on the most recent activity of our research group, the aim of the present talk is to give a critical overview of novel micro or nanoscale biosensors for the detection of cancer biomarkers, consisting in tumour associated antigens or gene mutations. Existing methods for cancer screening are still invasive, complex and quite expensive, being based on tissue sampling and cell morphology examination. Bioaffinity tests are instead based on simple and rapid detection of a wide range of biomarkers such as DNA mutations, RNA small sequences (micro-RNA), proteins (enzymes and glycoproteins), hormones and other kind of molecules. Thus, the combination of nanomaterials with such bio-assays offer the possibility of tailoring optimal sensing devices able to facilitate disease diagnosis (molecular diagnostics) as well as therapies optimisation (theranostics).

We have employed nanotechnology to develop small, fast, low-cost, ultrasensitive and highly specific biosensors for next-generation gene chips, based on different miniaturisation pathways. Carbon nanotube as well as magnetic nanoparticle-modified electrodes have been designed and tested for the detection of micro-RNA and DNA mutations. Gold nanoparticles have been synthesised and functionalised with antibodies and affibodies specific for tumor markers sensing. Moreover, polymeric nanotube arrays have been constructed for chemical grafting with new mimetic bioreceptors for clinically relevant analytes monitoring.Different immobilisation chemistries have been investigated by introducing functional groups (e. g. –OH, -COOH, -NH_2) suitable for each nanomaterial in order to assure high reactivity, orientation, accessibility and stability of the surface-confined receptors as well as for minimising non-specific adsorption events.

This talk will finally look into some recent advances of nanobiosensor by analyzing the trends, limitations, challenges and commercial devices in the field of clinical diagnostics.

10:00 Keynote lecture

Redox Reactions at Nanodiamond Surfaces Revealed by Attenuated Total Reflectance InfraRed Spectroscopy

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Nanodiamond (ND) is formed by detonation of carbon-based explosives and consists of individual diamond nanoparticles of ~ 5 nm in diameter. This material is attracting much interest at present in possible biomedical applications such as drug delivery, intracellular imaging and biosensing. Our interest lies in its unexpected redox properties [1,2] as we find that when immobilized on an electrode it is able to undergo direct oxidation and reduction and can also undergo electron transfer with solution redox molecules such as $IrCl_6^{2-}$. As undoped diamond is an insulating material, with a band gap of 5.5 eV we have suggested that this redox activity must be associated with its surface. By necessity bonding at the surface is unsaturated and due to the acid treatment used in purification highly oxidized. The ND surface contains an array of different surface functionalities, such as carboxylic acid, alcohols, quinones and ketones etc. As these groups can undergo redox transformations they may be responsible for the observed redox activity.

This talk will discuss recent experiments to elucidate the mechanisms behind electron transfer at the ND surface. This study uses Attenuated Total Reflectance InfraRed (ATR IR) spectroscopy to monitor changes in the vibrational frequencies of the surface functional groups of the ND in the presence of redox probes. In ATR IR the IR beam is directed through an internal reflection element (IRE), on top of which a thin layer of the nanomaterial is immobilised. The IR beam is reflected internally at the surface of the IRE, but the beam also penetrates the immediate environment above the prism surface as an evanescent wave. An IR vibration spectrum of the material within range of the evanescent wave can therefore be obtained and as only a thin layer is probed, solvent absorption is minimised. Use of nanomaterials ensures that a high surface area is available to be probed, allowing good quality IR spectra of the redox-active surface functional groups to be obtained.

[1] *Electrochemistry of Undoped Diamond Nanoparticles: Accessing Surface Redox States,* K. B. Holt, E. Millan-Barrios, D. J. Caruana, J. Am. Chem. Soc., (2009) 131, 13272+.

[2] *Undoped diamond nanoparticles: origins of surface redox chemistry,* K. B. Holt, Phys. Chem. Chem. Phys., (2010) 12, 2048

10:20 Short communication

Piezomicrogravimetric chemosensor for determination of selected alkaloids with dedicated porphyrin polymer film as recognition unit

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Two novel zinc porphyrins substituted with three electropolymerizable *N,N*-diphenylamines and either one or two acetamide side "arms" were synthesized for selective recognition of nicotine, cotinine, and myosmine. Subsequently, thin films of the porphyrin polymers were deposited on quartz crystal resonators by electrochemical polymerization under potentiodynamic conditions in order to fabricate a piezomicrogravimetric chemosensor. Spectral and electrochemical properties of the films as well as their surface morphology were characterized. Spectral results in combination with quantum mechanical calculations at the DFT level allowed for characterization of the polymer structure. They indicated that the porphyrin macrocycles remain essentially intact during electropolymerization for both porphyrin monomers used, as required for successful polymer application as the recognition unit in the chemosensor. Polymerization of the monomer bearing two and one acetamide "arm" resulted in films differing in morphology, porosity, and cross-linking. Electrochemical polymerization of the monomer bearing two acetamide arms apparently resulted in the film with more open structure than that of the film prepared by electropolymerization of the monomer with only one acetamide arm. The alkaloid interactions with the porphyrin polymer films were studied by using piezomicrogravimetry under flow-injection analysis conditions. All studied alkaloids bound reversibly to the porphyrin units of the polymers. For both porphyrins, nicotine binding was favored over binding of other alkaloids. Finally, analytical parameters of the devised piezomicrogravimetric chemosensor for alkaloid determination were evaluated.

Coffee break
Tuesday morning, 8 November, 10:35

Morning Session 2
Tuesday morning, 8 November, 11:00
Chair: Lewenstam and Holt

11:00 Keynote lecture

Solid-core and hollow magnetic nanostructures: synthesis, surface modifications and biological applications

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In the past decade, the synthesis of nanostructures of various geometries, chemical and physical behaviour has been intensively developed not only for its fundamental scientific interest but also for many technological, biosensing and medical applications, such as contrast increase of MRI, in bioaffinity assays, and targeted drug delivery. These structures have also unusual optical, electrical and catalytic properties, which allow for their potential and exciting applications in the above areas. In this respect I will focus on two types of representatives of such structures: magnetic nanoparticles and hollow polymeric nanocapsules. For the first type of nanostructures, I will discuss on the attachment of molecular adlayers to the surface of various types of nanoferrites for the purpose of their stabilisation, changing the hydrophilic/hydrophobic balance or to provide their surface with suitable functional groups ready for further modifications and tailoring, e.g., for targeted drug delivery. For the case of the second type of nanostructures, a considerable stress is laid on synthesis and characterization of hollow polymeric structures in which different molecules or particles can be entrapped or encapsulated. We have recently developed several new methods of preparation of polymeric micro- and nanocapsules using gaseous, liquid or solid particles that template growth of 3D structures The role of such capsule is to provide proper environment for molecules and nanoparticles and to protect them from degradation when they travel through the tissues to the targeted site. Moreover, the capsules allow much higher loading densities of the drug molecules when compared to e.g., covalent grafting on nanoparticle surface. Additionally, polymer shells influence the antifouling characteristics of the nanoparticles and also contribute to their effective hydrodynamic size, one of the key factor in avoiding the response by the ReticuloEndothelial System (RES).

11:20 Short communication

Comparison of techniques for determination of nanoparticle diameter

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Nanoparticles are studied in different fields of sciences [1]. In our laboratory we exploit gold nanoparticles (AuNPs) to promote direct electron transfer between planar electrodes and enzymes [2]. In all studies it is important to know the average size of nanoparticles (NPs). In this study we compared several techniques for NP size determination, specifically, Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Surface Plasmon Absorbance (SPA). Nine batches of AuNPs were prepared by well known citrate reduction method with average NP diameter ranging between 15 and 100 nm [3]. The results are summarized in the figure

b e l o w .

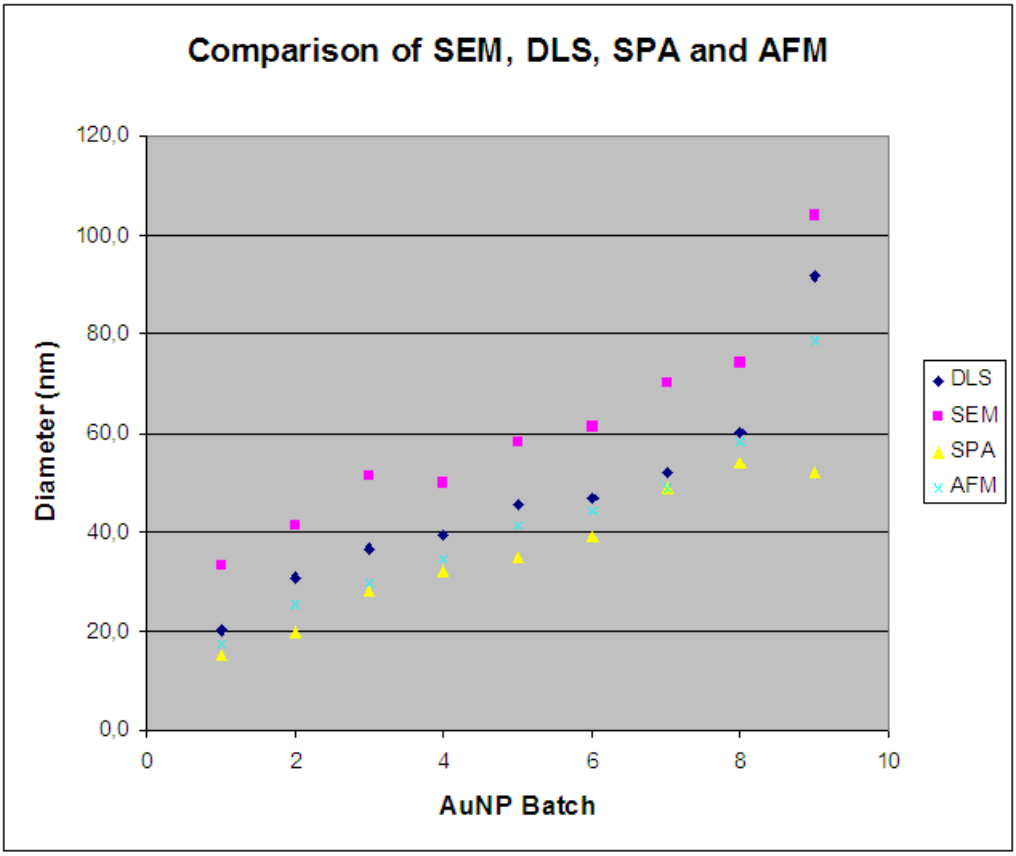

Fig. Average diameters of nine AuNP batches measured with DLS, SPA, SEM and AFM.

The four different techniques yielded AuNP diameters with systematic differences. SEM showed the largest and SPA the smallest diameter for the same batch of AuNPs. The discrepancy in NP diameter could be because the mentioned techniques measure different aspects of the NPs. The main conclusion was that using several techniques to estimate NP size might provide a better understanding about their size and shape.

REFERENCES

1. Whyman, R., *Gold nanoparticles a renaissance in gold chemistry*, 1996. Gold Bulletin **29**(1): p. 11-15.
2. Dagys, M., et al., *Laccase-gold nanoparticle assisted bioelectrocatalytic reduction of oxygen*, 2010. Electrochemistry Communications **12**(7): p. 933-935.
3. Turkevich, J., P.C. Stevenson, and J. Hillier, *A study of the nucleation and growth processes in the synthesis of colloidal gold*, 1951. Discussions of the Faraday Society **11**: p. 55-75.

11:35 Short communication

Electrodeposition method for preparing SERS- and LSPR-active platforms

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Novel biosensing methods, including Surface Enhanced Raman Spectroscopy (SERS) and Localized Surface Plasmon Resonance (LSPR), involves using of noble metal nanoparticles. The signal detected depends on nanoparticles size and shape, interparticle distance and refractive index of surrounding media.[1] Many attempts have been made to produce cheap, efficient and reproducible substrates.[2-6]

We present a universal biosensing platform for virus or antibody label-free recognition. It was produced using electrodeposition of silver nanoparticles onto tin-doped indium oxide (ITO) by cyclic voltammetry. Our method is consistent with the principles of green chemistry. Morphology of substrates was changed with tuning the scan rate of the applied potential and the number of scans. The platform is suitable both for surface enhanced Raman spectroscopy (SERS) and localized surface plasmon resonance (LSPR). The obtained substrates are reproducible and stable. Efficacy of our AgNPs substrate for biosensing was demonstrated for the detection of neurotransmitters such as choline at low concentration and with short detection time at SERS and for detection of specific binding between avidine and biotinylated bacteriophages at both SERS and LSPR.

[1] B. Sepúlveda, P.C. Angelomé, L.M. Lechuga, L.M. Liz-Marzán, LSPR-based nanobiosensors, Nano Today, 4 (2009) 244-251.
[2] M.E. Stewart, C.R. Anderton, L.B. Thompson, J. Maria, S.K. Gray, J.A. Rogers, R.G. Nuzzo, Nanostructured Plasmonic Sensors, Chemical Reviews, 108 (2008) 494-521.
[3] K.M. Mayer, J.H. Hafner, Localized Surface Plasmon Resonance Sensors, Chemical Reviews, 111 (2011) 3828-3857.
[4] A. Abbas, M.J. Linman, Q. Cheng, New trends in instrumental design for surface plasmon resonance-based biosensors, Biosensors and Bioelectronics, 26 (2011) 1815-1824.
[5] X. Hou, Y. Fang, Investigation of p-hydroxybenzoic acid from a new surface-enhanced Raman scattering system, Journal of Colloid and Interface Science, 316 (2007) 19-24.
[6] Y. Hu, Y. Song, Y. Wang, J. Di, Electrochemical synthesis of gold nanoparticles onto indium tin oxide glass and application in biosensors, Thin Solid Films, 519 (2011) 6605-6609.

11:50 Short communication

Free-radical adsorption as a method of binding gold nanoparticles to gold electrode surfaces.

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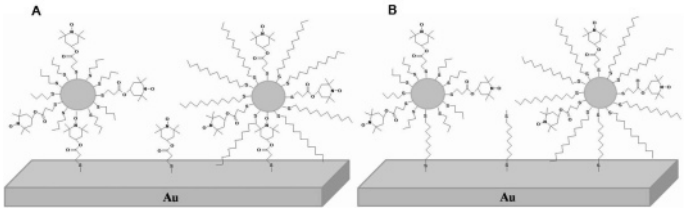
Stable free radicals TEMPO (2,2,6,6-tetramethyl-1-piperidine-1-oxyl) and its derivatives have been widely employed as spin labels [1], spin traps [2] and antioxidants [3] in the biomedical field, as mediator in „living" free radical polymerization [4], and as catalysts in aerobic oxidation processes [5]. The TEMPO radicals can also interact with gold electrode surface or gold nanoparticles and create the Au-NO bonding[6, 7].

Nanoparticles modified with single–component TEMPO-Thiol monolayer and mixed monolayers composed of bis[2-(4-oxy-2,2,6,6-tetramethylpiperidine-1-oxyl)ethyl] disulfide (TEMPO-DiSS) and alkanethiols (with four or twelve methylene groups) were synthesized[8]. Electrochemical behavior of the three types of NPs was studied, and their diffusion coefficients in solution and surfaces coverages were determined. We found that the interaction between

gold and TEMPO nitroxyl radicals may be useful as a method of binding gold nanoparticles to gold electrode surfaces.The nanoparticles were adsorbed on bare gold electrodes, and on the TEMPO-Thiol (Rys. A), or 1,9-nonanedithiol (Fig. B) modified gold electrode. Using cyclic voltammetry (CV), scanning tunneling microscopy (STM) and infrared spectroscopy (IR), we could compare the properties of the gold nitroxyl radical interaction with the well known gold- sulfur bonding.



1. P. P. Borbat, J. Costa-Filho,K. A. Earle, J. K. Moscicki,J. H. Freed, *Science***2001**, 291, 266-269.
2. R. P. Mason, *Free Radical Biol. Med.***2004,** 36, 1214-1223.
3. J. B. Mitchell, M. C. Krishna, P. Kuppusamy, J. A. Cook, A. Russo, *Exp. Biol. Med.***2001**, 226, 620-621.
4. C. J. Hawker, A. W. Bosman, E. Harth, *Chem. Rev.***2001**, 101, 3661-3688.
5. F. Minisci, F. Recupero, G. F. Pedulli, M. Lucarini, *J. Mol. Catal. A***2003**, 204-205, 63-90.
6. Z. Zhang, A. Berg, H. Levanon, R. W. Fessenden, D. Meisel, *J. Am.Chem. Soc.* **2003**, 125, 7959-7963
7. P. Krukowski, P. J. Kowalczyk, P. Krzyczmonik, W. Olejniczak, Z. Klusek, M. Puchalski, K. Gwozdzinski, *Applied Surface Science***2009**, 255, 3946–3952
8. O. Swiech, N. Hrynkiewicz-Sudnik, B. Palys, A. Kaim, R. Bilewicz, *J Phys Chem C***2011**, 115, 7347-7354.

12:05 Short communication

Carbon Nanoparticle Surface Modification for Sensor Development

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Emperor 2000® carbon nanoparticles are a form of carbon black with surface sodium sulfonate groups. This negative surface coverage is initially converted to positive amine functionality with reaction with a diamine. [1] The aminated carbon nanoparticles can then be subjected to further synthetic reactions.

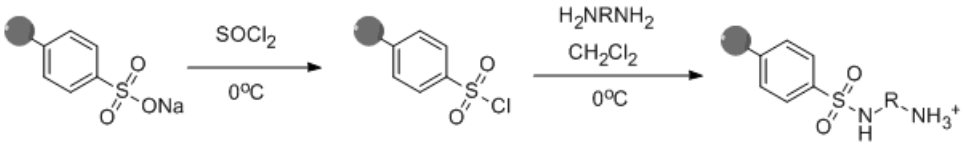

Figure 1. Diamine functionalisation of Emperor 2000® CNPs [1].

Carbodiimide mediated peptide coupling reactions were employed and a range of small organic molecules were reacted with the aminated surface of the carbon nanoparticles. This resulted in a range of carbon nanoparticles with new surface functionality created *via* amide bond formation.

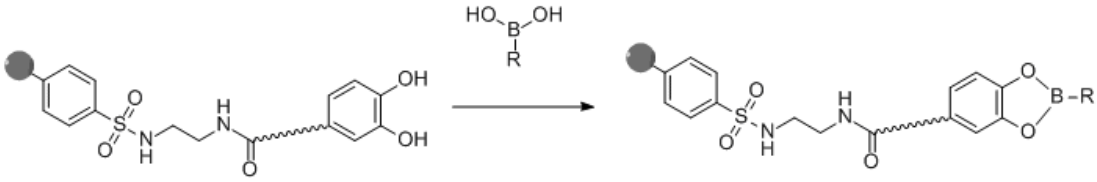

Figure 2. Boronic acid binding to terminal diol

By appending molecules with a free catechol unit to the carbon nanoparticles, there is the potential for them to be used for sensing applications.

Dopa-modified carbon nanoparticles have successfully demonstrated pH dependence which has been applied to gas pH sensing. [2] The modified nanoparticles have also been used detect boronic acids as the reaction of catechols and boronic acids is very favourable. [3]

[1] Watkins JD, Lawrence R, Taylor JE *et al.Physical Chemistry Chemical Physics* 12 (2010) 4872

[2] Ibrahim NB, Lawrence K, Xia F, James TD, Marken F *manuscript submitted to Sensors and Actuators B - Chemical* (2011)

[3] Lorand JP, Edwards JO *Journal of Organic Chemistry* 24 (1959) 769

12:20 Tutorial lectore

Impedance Methods in Electrochemistry

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Lunch break
Tuesday afternoon, 8 November, 13:00

Departure
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Index

I

J

K

L

M

N

O

P

Q

R

S

T

V

W

Y

Z