Surface Modification for Chemical and Biochemical Sensing

SMCBS 2015

THE 7TH INTERNATIONAL WORKSHOP ON SURFACE MODIFICATION FOR CHEMICAL AND BIOCHEMICAL SENSING

Organized by

Institute of Physical Chemistry
Polish Academy of Sciences
Kasprzaka 44/52
01-224 Warsaw, Poland

Pułtusk Castle, November 6 – 10, 2015

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The Bioelectrochemical Society

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of electrochemical concepts
in biochemistry/ bioanalysis
and
fundamental or applied studies
of biological systems

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Acknowledgements

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We are pleased and honoured to present this Programme of the 7th International Workshop on Surface Modification for Chemical and Biochemical Sensing organised by Institute of Physical Chemistry of the Polish Academy of Sciences. In the spirit of the previous workshops of this series we are especially happy to welcome numerous short communications and posters presented by young researchers. We are proud that over a dozen distinguished scientists have accepted our invitations to deliver tutorial lectures and are ready for further discussions with participants, and young researchers in particular.

With an increasingly complex chemical environment, our research is more focused on the development of new sensing devices. Modified surfaces are their important parts. Contemporary trends go towards increasing both the sensitivity and selectivity control over certain properties of the sensing surface. This direction of research requires collaboration not only from the fields of chemistry and biology, but also from physics, materials science, electronics, etc. Although the SMCBS workshops continues to be mainly focused 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 workshops in the SMCBS series organised in Białowieża (2003), Kazimierz Dolny (2005), Włodowice (2007), Przegorzały (2009), Łochów (2011) and Łochów (2013), 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 concepts and collaborations. This is especially important as European Union funding is becoming larger part of our research budgets. We are very happy to see again our friends. Some of them participated in this series of workshops from the very beginning. They significantly contributed to making our workshop a permanent position in our overloaded conference calendar.

The Organising and Programme Committee is grateful to all those who contributed to the present Workshop. We are particularly thankful to participants presenting their contributions, session chairpersons and the members of the International Scientific Advisory Board. Last not least, we are grateful to our sponsors.

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 2015

Organizers

The Workshop is organized by
the Institute of Physical Chemistry of the Polish Academy of Sciences,
Kasprzaka 44/52, 01-224 Warsaw, Poland.

International Scientific Advisory Board

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- Francis D'Souza (University of North Texas, Denton, TX, USA)
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- Wolfgang Schuhmann (Ruhr-Universitat Bochum, Bochum, Germany)
- Gunther Wittstock (Carl von Ossietzky Universitat Oldenburg, Oldenburg, Germany)

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- Chair persons:
  Włodzimierz Kutner and Marcin Opałło (Institute of Physical Chemistry, Warsaw, Poland)

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Pułtusk Castle November 6 – 10, 2015

SMBCS'15 Program

2015-11-06, Friday

13:00 – 19:00	**Transfer to Pułtusk / Arrival**
19:00 – 20:00	**Dinner**

20:00 – 21:40 **Evening Session**
(chairs: Pawel Kulesza, Elena Ferapontova)

20:00 – 20:40	T01	**Pawel Kulesza** Development of nanostructured hybrid materials for electrocatalytic, bioelectrocatalytic and photoelectrocatalytic reduction of carbon dioxide
20:40 – 21:00	K01	**Munetaka Oyama** Surface modification of metal nanoparticles using a just immersion approach
21:00 – 21:40	T02	**Elena Ferapontova** Molecular and interfacial aspects of nucleic acid electrochemistry

21:50 – 22:30	**Poster Immobilisation**

2015-11-07, Saturday

08:00 – 09:00		**Breakfast**
09:00 – 10:30		**Morning Session 1** (chairs: Alexander Kuhn, Klaus Mathwig)
09:00 – 09:40	T03	**Alexander Kuhn** The fundamentals of bipolar electrochemistry and its application to controlled surface modification
09:40 – 10:00	K02	**Klaus Mathwig** Electrochemical stochastic amperometry and spectroscopy in nanofluidic devices
10:00 – 10:15	SC01	**Shokofueh Rastgar** Photo-induced electron transfer study of $BiVO_4$ nanoparticles adsorbed at molecular soft interfaces: Application to photo-catalytically oxidation of water
10:15 – 10:30	SC02	**Zbigniew Stojek** Assembling paramagnetic ceruloplasmin at electrode surface covered with ferromagnetic nanoparticles. Scanning electrochemical microscopy in presence of magnetic field
10:30 – 11:00		**Coffee Break**
11:00 – 12:55		**Morning Session 2** (chairs: Andrzej Lewenstam, Liza Rassaei)
11:00 – 11:40	T04	**Andrzej Lewenstam** Application driven research in sensor technology, Novel multisensor platforms for monitoring of ion-transport through biological membranes
11:40 – 12:00	K03	**Levi Gheber** Towards portable, deployable, arrayed biosensors
12:00 – 12:20	K04	**Ievgen Mazurenko** H_2/O_2 biofuel cells: Macro-structured conductive supports to enhance power cell
12:20 – 12:35	SC03	**Veronika Ostatna** Utilization of carbon electrodes in label-free analysis of proteins
12:35 – 12:55	K05	**Liza Rassaei** Electrosynthesis of metal organic frameworks: ZIF-8/ZnO nanohybrids
13:00 – 14:30		**Lunch**

14:30 – 16:25		**Afternoon Session 1** (chairs: Renata Bilewicz, Gunther Wittstock)
14:30 – 15:10	T05	**Renata Bilewicz** Model lipid membranes prepared by Langmuir-Blodgett-Shaefer technique under influence of drugs and drug carriers
15:10 – 15:30	K06	**Ilaria Palchetti** Label and label-free electrochemical biosensing platforms for microRNA detection
15:30 – 16:10	T06	**Gunther Wittstock** Nanoparticle imprinted polymers
16:10 – 16:25	SC04	**Palanisamy Kannan** Carbon nanotubes supported Escherichia Coli for electrocatalysis of volatile organic compounds
16:25 – 16:50		**Coffee Break**
16:50 – 18:45		**Afternoon Session 2** (chairs: Francis D'Souza, Lars Jeuken)
16:50 – 17:30	T07	**Francis D'Souza** Graphene surface decorated with biomimetic donor-acceptor dyads for modulating of electron transfer dynamics
17:30 – 17:50	K07	**Paul Millner** Molecular engineering; how surface design at the nanoscale influences the performance of biosensors, and smart nanoparticles
17:50 – 18:05	SC05	**Joanna Niedziolka-Jonsson** Metallic nanostructures for virus detection and determination
18:05 – 18:25	K08	**Lars Jeuken** Membrane-modified electrodes for the study of proton-pumping enzymes and membrane-bound hydrogenases
18:25 – 18:45	K09	**Gerd-Uwe Flechsig** Heated electrochemical DNA sensors for molecular diagnosis of genetic defects and infectious diseases
19:00 – 20:00		**Dinner**
20:00 – 22:00		**POSTER SESSION**

2015-11-08, Sunday

08:00 – 09:00	Breakfast

09:00 – 10:30 **Morning Session 1**
(chairs: Sergey Shleev, Nikolaos N. Daskalakis)

09:0 – 09:40	T08	**Sergey Shleev** Electric power biodevices
09:40 – 10:00	K10	**Nikolaos N. Daskalakis** Quantitative lateral flow assay for monitoring of kidney disease
10:00 – 10:15	SC06	**Piotr Warszynski** Multifunctional hybrid ultrathin polyelectrolyte coatings
10:15 – 10:30	SC07	**Paweł Weronski** Application of rotating disk electrode technique in studies of supported thin films of spherical particles

10:30 – 11:00	**Coffee Break**

11:00 – 12:55 **Morning Session 2**
(chairs: Izabella Brand, Bozena Sikora)

11:00 – 11:40	T09	**Bozena Sikora** Opto-magnetic nanoparticles for biological applications
11:40 – 12:00	K11	**Lubomir Svorc** A state-of-the-art on chemical modification of boron-doped diamond electrodes for applications to biosensors and biosensing
12:00 – 12:20	K12	**Izabella Brand** In situ detection of molecular scale changes induced in model membranes due to lipid – protein interactions
12:20 – 12:35	SC08	**Stanislav Trashin** Attaching of redox proteins on electrodes by “gluing” with oligosilanes for direct electron transfer
12:35 – 12:55	K13	**Sarah Horswell** Electrochemical and infrared studies of phospholipid bilayers supported on Au(111) surfaces

13:00 – 14:00	**Lunch**

14:30 – 16:10 **Afternoon Session 1**
(chairs: Ambra Giannetti, Karsten Haupt)

14:30 – 15:10	T10	**Karsten Haupt** Molecularly imprinted polymer nanogels and nanocomposites as plastic antibody mimics for bioimaging and theranostics
15:10 – 15:50	T11	**Ambra Giannetti** Fluorescence based optical biosensors
15:50 – 16:10	K13b	**Patrizia Mussini** Inherently chiral electrodes, the effective tool for chiral voltammetry

17:00 – 20:00	**Castle exploration with treasure hunting**
21:30 – 23:00	**Dinner/Banquet**

2015-11-09, Monday

08:00 – 09:00 **Breakfast**

09:00 – 10:30 **Morning Session 1**
(chairs: Roberto Guzman, Gary Blanchard)

09:00 – 09:40	T12	**Gary Blanchard** Molecular motion as a probe of interface structure. Application from LB films to plasma membranes
09:40 – 10:00	K14	**Roberto Guzman** Controlled drug delivery with polymeric nanoparticles: synthesis, modeling and application in vitro and in vivo pancreatic cancer
10:00 – 10:15	SC09	**Gulnara Safina** Macroporous Indium-Tin Oxide as a Platform for Biosensing Applications
10:15 – 10:30	SC10	**Marc Riedel** Chemisorbed DNA-layer for impedimetric DNA detection: Influence of DNA length and Overhang orientation on the hybridization signal

10:30 – 11:00 **Coffee Break**

11:00 – 12:55 **Morning Session 2**
(chairs: Tan Phat Huynh, Wolfgang Schuhmann)

11:00 – 11:40	T13	**Wolfgang Schuhmann** Harvesting bioenergy - biofuel cells and photobiovoltaics
11:40 – 12:00	K15	**Tan-Phat Huynh** Flexible multi parametric sensors with self-healing properties
12:00 – 12:20	K16	**Caroline Canizzo** Nanostructured and functionalized screen printed electrodes for the detection of metallic pollutants in water
12:20 – 12:35	SC11	**Agata Pomorska** In-situ monitoring of polymer brush film growth on gold as a function of solvent composition by means of Quartz Crystal Microbalance
12:35 – 12:55	K17	**Jingyuan Chen** Current-voltage curves at various diameters of single nanoelectrodes

13:00 – 14:30 **Lunch**

14:30 – 16:05 **Afternoon Session 1**
(chairs: Elena Ferapontova, Arkady Karyakin)

14:30 - 15:10	T14	**Arkady Karyakin** Advanced biosensors for non-invasive diagnostics
15:10 – 15:30	K18	**Nicolas Plumere** Mechanism for protection of O_2 sensitive catalyst in redox hydrogels
15:30 – 15:50	K19	**Mathieu Etienne** Some strategies for tuning the interaction between bacteria and (nano)materials in electroactive biocomposites
15:50 – 16:05	SC12	**Tomasz Rebis** Redox-active lignosulfonate/conducting polymer composites. Characterization and electroanalytical properties

16:05 – 16:30 **Coffee Break**

16:30 – 17:40 **Afternoon Session 2**
(chairs: Karsten Haupt, Jahangir Rather)

16:30 – 16:50	K20	**Claire Rossi** EGFR inhibition by curcumin in cancer cells: a dual mode of action - biomimetic and cellular
16:50 – 17:05	SC13	**David Pally** Functionalization of glassy carbon electrode by amines electrochemical oxidation for micro-pollutants detection in water
17:05 – 17:25	K21	**Pawel Krysinski** Effect of Iron Oxide-Based Magnetic Nanocarriers on Model Biomimetic Membranes: Electrochemical and Spectroscopic Studies
17:25 – 17:40	SC14	**Jahangir Rather** Facile Hydrothermal Synthesis of In_2O_3Nanoboxes: Swift Sensing of Parabens

19:00 – 20:00 **Dinner**

21:00 – ? **Disco!**

2015-11-09, Tuesday

08:00 – 09:00	**Breakfast**

09:00 – 10:10 **Morning Session 1**
(chairs: Frank Marken, Piyush Sindhu Sharma)

09:00 – 09:40	T15	**Frank Marken** Intrinsically microporous films and membranes in electrochemistry
09:40 – 9:55	SC15	**Alexandra Lipka** Investigation of the Protease-activated Receptor (PAR)1 on Thrombocytes using Single Molecule Force Spectroscopy
09:55 – 10:10	SC16	**Piyush Sindhu Sharma** Electrochemically Synthesized Molecularly Imprinted Polymers for Selective Determination of Biomarker Compound

10:10 – 10:30	**Coffee Break**

10:30 – 11:40 **Morning Session 2**
(chairs: Andreas Ebner, Lo Gorton)

10:30 – 10:50	K22	**Andreas Ebner** Sensing Molecular Interactions in Nanomedicine on the Single Molecule Level
10:50 – 11:30	T16	**Lo Gorton** Bioelectrochemical studies of photosynthetic cells and membranes on electrodes
11:30 – 11:40		**Closing**

12:00 – 13:00	**Lunch**
13:00 –	**Departures**

2015-11-06, Friday

13:00 – 19:00	**Transfer to Pułtusk / Arrival**
19:00 – 20:00	**Dinner**

20:00 – 21:40 **Evening Session**
(chairs: Pawel Kulesza, Elena Ferapontova)

20:00 – 20:40	T01	**Pawel Kulesza** Development of nanostructured hybrid materials for electrocatalytic, bioelectrocatalytic and photoelectrocatalytic reduction of carbon dioxide
20:40 – 21:00	K01	**Munetaka Oyama** Surface modification of metal nanoparticles using a just immersion approach
21:00 – 21:40	T02	**Elena Ferapontova** Molecular and interfacial aspects of nucleic acid electrochemistry

21:50 – 22:30	**Poster Immobilisation**

T01. **Development of Nanostructured Hybrid Materials for Electrocatalytic, Bioelectrocatalytic and Photoelectrocatalytic Reduction of Carbon Dioxide**

Pawel J. Kulesza*, Ewelina Seta, Anna Wadas, Ewelina Szaniawska, Renata Solarska, Krzysztof Bienkowski, Weronika Lotowska, Iwona A. Rutkowska

Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland.

*pkulesza@chem.uw.edu.pl

There has been growing interest in the electrochemical reduction of carbon dioxide, a potent greenhouse gas and a contributor to global climate change, and in its conversion into useful carbon-based fuels or chemicals that include carbon monoxide, oxalate, formate, carboxylic acids, formaldehyde, acetone or methanol, in addition to various hydrocarbons at different ratios. Given the fact that the CO2 molecule is very stable, its electroreduction processes are characterized by large overpotentials. To produce highly efficient and selective electrocatalysts, the transition-metal-based molecular materials are often considered. It is believed that, during electroreduction, the rate limiting step is the protonation of the adsorbed CO product to form the CHO adsorbate.

Because reduction of CO2 can effectively occur by hydrogenation, to optimize the conventional electrocatalytic approach, we propose nanostructured metallic palladium in a form of highly dispersed and reactive nanoparticles generated within supramolecular network of N-coordination complexes. Reduction of carbon dioxide begins now at less negative potentials and is accompanied by significant enhancement of the CO2-reduction current densities. Among important issues are specific interactions between nitrogen coordinating centers and metallic palladium sites at the electrocatalytic interface.

A challenging alternative is to explore ability of biofilms to form hydro-gel-type aggregates (held together by extracellular polymeric substances, EPS) of microorganisms attached to various surfaces including those of carbon electrode materials. Biofilms are able to transfer electrons to and from electrodes, and they can act in a manner analogous to redox or conducting polymer films on electrodes. We have recently demonstrated that it is possible to drive catalytic electrode reactions (e.g. oxygen reduction) using the hybrid (composite) layers composed of aggregates of bacteria. Here we have explored a biofilm formed by a strain of Yersinia enterocolitica; it is characterized by a high physicochemical stability over wide ranges of pH (4-10) and temperatures (0-40°C). Upon incorporation of various noble metal nanostructures and/or conducting polymer ultra-thin films, high reactivity toward CO2-reduction is observed.

Another possibility to enhance electroreduction of carbon dioxide is to explore direct transformation of solar energy to chemical energy using transition metal oxide semiconductor materials. We show here that, by intentional and controlled combination of metal oxide semiconductors, we have been able to drive effectively photoelectrochemical reduction of carbon dioxide. The combination of titanium (IV) oxide (TiO2) and copper (I) oxide (Cu2O) has been explored toward the reduction of carbon (IV) oxide (CO2) before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH3OH), as demonstrated upon identification of final products using conventional and mass-spectrometry assisted gas chromatography. On mechanistic grounds, the role of TiO2 seems to be not only stabilizing: the oxide is also expected to prevent the recombination of charge carriers.

K01. **Surface Modification with Metal Nanoparticles Using a Just Immersion Approach**

Munetaka Oyama

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Metal nanoparticles (NPs) have been attracting active attention as functional units for electrode surface modifications because they can change the electronic communications on the conductive materials. In this decade, my group studied verious modifications of metal NPs on electrode surfaces. Started from the use of indium tin oxide (ITO) electrodes (1), some other trials are now in progress, seeking new possibilities and functions of metal NPs. The key strategy of our trials is the attachment of small metal NPs via physisorption accomplished by just immersing a substrate into a solution of small metal NPs (2). Some recent results as follows will be presented in the meeting.

Metal nanoparticle-modification on ITO electrodes : My group is proposing a simple methodology to modify electrode surfaces with metal NPs applying a seed-mediated growth method. With this approach, nanostructuring on ITO surfaces are possible and the electrochemical properties can be compared, for example, for the electrocatalytic oxidation of uric acid (3).

Use of paper supports for modifying metalNPs: As a unique trial, we used paper materials such as Kimwipes and cotton gauze to fix metal NPs in the vicinity of the base electrode surface. We could observe significant improvement of the electron transfer reactions of ferrocyanide with the use of gold NPs modified Kimwipes (4).

Gold NPs-modified metal electrodes: We are studying some combinations of metal NPs with metal electrodes. Among them, we could observe the electrocatalytic oxidation of water, in particular, in alkaline solutions with a gold nanoseed modified Pd electrode (5). As another combination of gold nanoseed particles (AuNSPs) with a metal base electrode, we observed some electrochemical properties of an AuNSP-attached Ni (AuNSP/Ni) electrode. Normally, a Ni electrode is not suitable for the cyclic voltammometric measurements of redox couples such as $Fe(CN)_6^{4-/3-}$. However, the AuNSP/Ni electrode has shown an impressive improvement of the electrochemical responses of $Fe(CN)_6^{4-/3-}$ in comparison with those with a Ni electrode (6).

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(2) Kambayashi, M.; Zhang, J.; Oyama, M. *Cryst. Growth Des.* **2005**, *5*, 81.
(3) Kajita, T.; Oyama, M. *J. Electroanal. Chem.* **2011**, *656*, 264.
(4) Nakashima, D.; Marken, M.; Oyama, M. *Electroanalysis* **2013**, *25*, 975.
(5) Nakayama, Y.; Oyama, M. *Chem. Commun.* **2013**, *49*, 5228.
(6) Uemoto, T.; Nakayama, Y.; Chen, X.; Chang, G.; Oyama, M. *Electroanalysis* **2015**, *27*, 964.

T02. **Interfacial Aspects of Nucleic Acid Electrochemistr**

Elena E. Ferapontova

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Highly specific interactions between DNA bases underlying unique biorecognition and electronic properties of DNA allow their challenging applications in bioelectronics, nanomachinery, and in sensor and actuator systems (1). In this context, fundamental studies of electron transfer (ET) reactions, underlying principles of operation of DNA-based electronics and electrochemical DNA biosensors and proceeding at the electrode-solution interface, are particularly important. These electrochemical ET studies are commonly performed with DNA molecules tethered to gold electrodes via alkanethiol linker and modified with redox-probes either conjugated to DNA or intercalated into the DNA duplex (Figure 1) (2,3).

Here, I overview our recent studies of ET mediated by the DNA π-stacked duplex, operating as a one-dimensional electronic conductor, and of ET in the redox probe-conjugated DNA duplexes triggered by the potential-induced diffusion of the redox probe to the electrode, including the ways of their optimisation by the proper choice of DNA probes and removal of the linker representing an extra barrier for ET (3-5). These results contribute to understanding of the fundamentals of ET reactions proceeding in the electrode-tethered DNA and design of advanced genosensor technologies exploiting differences in electrochemical properties of single stranded (ss) and double stranded (ds) DNA (2,6). Current trends in construction of label-free electrochemical genosensors for cancer diagnosis, exploiting differences in electrochemical properties of ss and ds DNA/RNA and RNA-aptamers and their complexes with cancer-related proteins will be discussed [7,8].

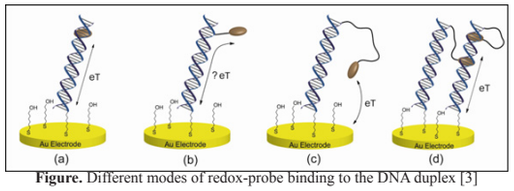

Figure. Different modes of redox-probe binding to the DNA duplex [3]

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(5) R Campos, A Kotlyar, EE Ferapontova. Langmuir 2014, 30, 11853–11857
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2015-11-07, Saturday

08:00 – 09:00 **Breakfast**

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16:50 – 18:45 **Afternoon Session 2**
(chairs: Francis D'Souza, Lars Jeuken)

16:50 – 17:30	T07	**Francis D'Souza** Graphene surface decorated with biomimetic donor-acceptor dyads for modulating of electron transfer dynamics
17:30 – 17:50	K07	**Paul Millner** Molecular engineering; how surface design at the nanoscale influences the performance of biosensors, and smart nanoparticles
17:50 – 18:05	SC05	**Joanna Niedziolka-Jonsson** Metallic nanostructures for virus detection and determination
18:05 – 18:25	K08	**Lars Jeuken** Membrane-modified electrodes for the study of proton-pumping enzymes and membrane-bound hydrogenases
18:25 – 18:45	K09	**Gerd-Uwe Flechsig** Heated electrochemical DNA sensors for molecular diagnosis of genetic defects and infectious diseases

19:00 – 20:00 **Dinner**

20:00 – 22:00 **POSTER SESSION**
Abstracts at page 140

T03. **The fundamentals of bipolar electrochemistry and its application to controlled surface modification**

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Bipolar electrochemistry is a somewhat unconventional way of performing electrochemical experiments, as it allows carrying out redox reactions on conducting objects in a wireless way, due to their polarization in strong electric fields. The concept has been known for decades (1), but undergoes currently a true renaissance in various scientific domains, with a wide range of applications, especially in the fields of analytical chemistry and materials science (2-4). This lecture will first treat some fundamental aspects of this attractive approach and then present an overview of some of the most recent advances in this field (5) with a special focus on the highly controlled surface modification of micro- and nanoobjects (6-13).

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K02. **Electrochemical stochastic amperometry and spectroscopy in nanofluidic devices**

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The miniaturization of lab-on-a-chip analytical systems allows fundamentally new approaches that are not possible with bulk techniques. By reducing the molecular reaction space to a nanochannel, small molecules can by sensed in novel ways. The effect of nanoscale confinement can both lead to improvement in practical sensing devices for point-of-care applications as well as for fundamental studies at the mesoscopic or single-molecule level.

In nanofluidic electrochemical sensors, only zeptomole quantities of redox molecules are detected. The molecules undergo redox cycling as they travel diffusively between two electrodes at opposing walls of a nanochannel. Thereby a highly amplified current is generated per molecule. In these sensors, the random Brownian walk of molecules diffusing in and out of the nanochannel leads to considerable number density fluctuations of the detected analytes. These fluctuations are directly mirrored in the detected Faradaic currents.

In this lecture, I will introduce the techniques of *stochastic amperometry*[1] and *electrochemical correlation spectroscopy*.[2] These are used to analyze fluctuations in order to determine the diffusion coefficient and reversible adsorptivity[3] of molecules.

So far, these methods have been employed mostly to detect ferrocenes or similar compounds with only a single possible electron-transfer process. Recently, they have been used to study also more complex ferrocenylthiophene molecules with several (two or three) well-resolved electrochemically reversible one-electron transfer processes. Therefore, it can be possible to determine molecular properties *at different redox states* in electrochemical nanogap sensors.

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SC01. **Photo-Induced Electron Transfer Study of Nanostructured $BiVO_4$ Adsorbed at Molecular Soft Interfaces: Application to Photo-Catalytically Oxidation of Water**

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Photo-induced electron transfer across two immiscible electrolyte solutions (ITIES) interfaces, with a photosensitizer and quencher located in different liquid phases has been proposed as a model system for natural photosynthesis and heterogeneous photo-catalysis [1-3]. Overall water splitting by a semiconductor photocatalyst has been studied largely applied in photon energy conversion and fuel production [4-6]. With the aim of developing new water splitting protocols, i.e. artificial photosynthesis, liquid/liquid interfaces represent defect free molecularly soft platform suitable for assembling of nanostructured based semiconductor photocatalysts [7].

Herein, water oxidation (or O_2 evolution) reaction, the most challenging part in the water splitting process, is studied in the presence of bismuth vanadate ($BiVO_4$) nanoparticles as a model for an O_2 evolution photocatalyst which is adsorbed at chemically polarized 1,2-dichlroethane/water interface. $[Co(bpy)_3](PF_6)_3$ is used as an electron acceptor and redox mediator in the organic phase. The photo-electrochemical response of $BiVO_4$ nanoparticles in the presence of organic soluble $[Co(bpy)_3]^{3+}$ is studied by Scanning Electrochemical Microscopy (SECM) technique, in which an ultramicroelectrode (UME) probe is placed in organic phase several micrometer above the interface. It measures the transient photocurrent responses based on electrochemical oxidation of $[Co(bpy)_3]^{2+}$ as a product of interfacial electron transfer process between $BiVO_4$ and $[Co(bpy)_3]^{3+}$ in the presence of light. By applying a step function in the light flux through an optical fiber (off-on), the effects of key experimental variables on the photocurrent are determined.

Finally, the results propose a promising strategy for significant improvement of $BiVO_4$ photoactivity for the O_2 evolution reaction in bulk solution.

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SC02. **Assembling Paramagnetic Ceruloplasmin at Electrode Surface Covered with Ferromagnetic Nanoparticles. Scanning Electrochemical Microscopy in Presence of Magnetic Field**

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The immobilization of active enzymes on electrode surfaces is an important step in bioelectrochemistry and electroanalysis. Correspondingly, there is a need for a reliable strategy allowing the characterization of the immobilized enzymes. In this respect scanning electrochemical microscopy was found to be a powerful tool for the investigation of enzyme-modified electrodes.[1,2] In contrast to the electrochemical methods typically used directly for the evaluation of the enzyme-modified electrodes, the local catalytic activity of the protein immobilized at the electrode surface may be examined from the solution side of the biointerface. By appropriately controlling the potential at the microelectrode SECM tip, the products or the reactants of the enzymatic reaction can be detected with high sensitivity and specificity.

In this contribution we demonstrate that a layer of ferromagnetic nanoparticles covering the gold electrode surface guarantees the immobilization of Cp in the preferred orientation and enhances the electrocatalytic activity of the paramagnetic Cp. If, simultaneously, a magnet is placed beneath the modified electrode, the activity of Cp will increase further; this was confirmed by the data obtained from the SECM- and the laser ablation coupled with an inductively coupled plasma mass spectrometry (LA ICPMS) experiments. The results acquired under various conditions suggested that both: the presence of Fe@C Nps on the Au surface and the presence of an outer, moderate magnetic field were necessary to assure the highest ferrooxidative activity of ceruloplasmin.[3]

The developed electrode architecture should be successful in the application of other paramagnetic proteins in the analytical work in solutions and the body fluids.[4]

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T04. **Application driven research in sensor technology - Novel multisensor platforms for monitoring of ion-transport through biological membranes**

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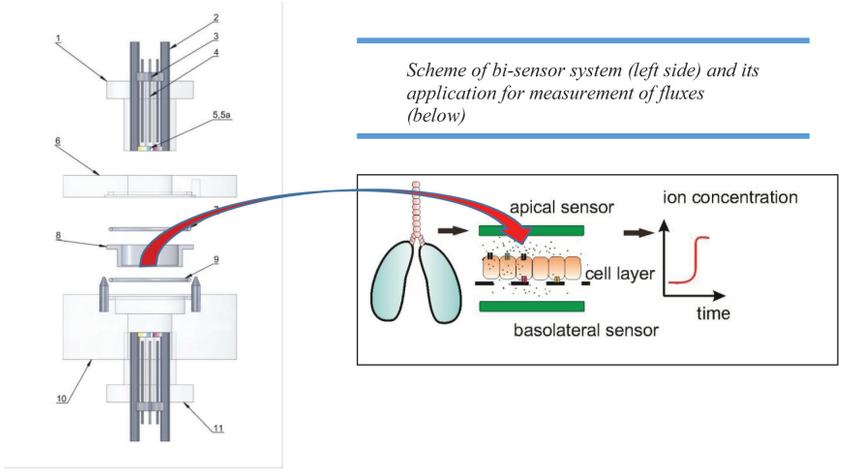
Multielectrode bi-sensor system designed for real-time concentration measurements of sodium, potassium, chloride and pH is an ultimate target of this tutorial. The system used for measurements in a small volume of biological liquid bathing a living human bronchial epithelial cell monolayer to characterize ion-fluxes (1).
Several application-driven research milestones allowing realization of bi-senors idea will be characterized. They include inventing solid-contact ion-selective electrodes, junctionless reference electrodes, one-drop measurement, and signal interpretation by Nernst-Planck-Poisson model. Support provided by recommendations for clinical diagnostic measurements will be as well employed.
Very recent results on dual-function reference electrodes that work as electrochemically active body for ion-sensors and biosensors will be used to show new perspectives and challenges.



Scheme of bi-sensor system (left side) and its application for measurement of fluxes (below)

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K03. **Towards portable, deployable, arrayed biosensors**

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Monitoring our environment for biological threats is a growing need, largely unmet. Currently, biosensing platforms suffer from a myriad of shortcomings, regarding various basic requirements, which ultimately lead to the same end-result: the need for trained, expensive human intervention and the transport of the technologies to large facilities.
One of the chief shortcomings of present technologies is the size of sensing elements. The smallest ones are produced by microarray technology: 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, a drastic reduction in sizes is required. While nano-biolithography techniques have the ability to fabricate structures of biomolecules as small as ~ 40 nm, the loss in Signal to Noise Ratio (SNR) accompanying miniaturization leads to very few examples of working biosensors of these sizes.
Autonomy of biosensing platforms requires vast integration of subsystems, like sample collection, purification, amplification, liquid handling, read-out, analysis and remote transmission of results. Such integration does not exist presently.The vast majority of biosensing systems use some form of labeling, for the detection of the bound target. Labeling is opposed to the concept of continuous monitoring of target levels in a sample. For this purpose label-free detection methods are being developed, so far with relatively poor sensitivity and specificity.
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 other optical methods, and integrating on-chip polymer microlenses-as part of the read-out system (9) and microfluidics for liquid sampling.
We present results from each of these, discuss the complex inter-dependencies between the various factors, and ways to overcome some difficulties.

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K04. H_2/O_2 biofuel cells: Macro-structured conductive supports to enhance power cell performances

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Enzymatic H_2/O_2 fuel cells (EFC) recently emerged as attractive devices for small power applications [1]. In this "green" fuel cell, biocatalysts would replace chemical catalysts both at the anodic and cathodic sides. We previously identified and purified a hyperthermophile [NiFe] hydrogenase with outstanding properties compared to classical [NiFe] hydrogenases. We proved it is very efficient for oxidizing H_2 over a large range of temperatures from 25 to 80 °C and is tolerant to O_2 and completely insensitive to CO [2]. Coupled to a very efficient cathode based on a thermostable bilirubin oxidase (BOD), a EFC was designed delivering 1.5 $mW.cm^{-2}$ at 0.6 V over a range of temperature from 30 to 80 °C [3].

One of the main challenges to EFC is to achieve higher performances and stability in order to become a self-sufficiency source of energy. H_2/O_2 EFC based on fish bone carbon nanofibers (CNFs) have proved that three main key challenges on enzyme immobilization have to be overcome: 1- Carbon nanofiber film stability on planar graphite electrodes which limits the available interacting surface; 2- substrate transport limitation through the mesoporous material; and 3- stability of the bio hybrid over time [3]. Recently we explored two different ways to overcome these limitations. We showed that gold nanoparticles can serve as efficient platforms for hydrogenase immobilization with enhanced long-term stability [4]. We also designed a H_2/O_2 EFC with an air-breathing cathode [5]. We present in this work, new strategies based on enzymes entrapped in carbon felt-based materials which act as enzyme host matrices with no need of additional electron collector. Catalytic oxidation of H_2 and reduction of O_2 will be analyzed using electrochemistry in terms of enzyme grafting, influence of carbon material modification with different nano-materials and biopolymers. Electrochemical analysis of the biohybrid stability will be linked to quantification of enzyme release and/or denaturation. Finally, we will develop a H_2/O_2 EFC demonstrator with the power cell efficiency required to feed a wireless electronic device.

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SC03. **Utilization of carbon electrodes in label-free analysis of proteins**

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Progress in proteomics and biomedicine opens the door for new methodologies.[1] Last decades we have been developing label-free and reagent-free electrochemical methods for protein and protein-nucleic acid interaction analysis.[2] Almost 15 years we studied peptides and proteins using constant current chronopotentiometric stripping analysis at Hg-containing electrodes. Well-developed peak H, due to the catalytic hydrogen evolution, displays sensitivity to local and global changes in protein structure.[2] In addition, we showed that oxidation peak of tyrosine and tryptophan at carbon electrodes can be used for label free structure-sensitive analysis of a large number of proteins, including those important in biomedicine, such as oncoprotein Anterior Gradient 2 (AGR2).[3] Systematical testing of different electrodes (edge and basal plane pyrolytic graphite, glassy carbon, carbon paste and screen-printed electrodes) indicated that using edge plane pyrolytic graphite electrode and glassy carbon electrode large differences in peak heights of native and denatured form of proteins could be observed.[4]

We also studied *His*-tagged and non-tagged forms of some proteins AGR2, Glutathione-S-transferase, α-synuclein and cytochrome b5.[5] *His*-tagged forms yielded characteristic electro-oxidation peak of *His* residues. Appearance of this peak was depended on the carbon electrode type.[5]

It can be expected that the method sensitive to protein structure, including oxidation *His* peak, in combination with Tyr and Trp oxidation responses, may become useful in biomedicine and proteomics.

This work was supported by Czech Science Foundation, 13-00956S project.

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K05. **Electrosynthesis of metal organic frameworks: ZIF-8/ZnO nanohybrids**

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Metal-organic frameworks (MOFs) as porous solid materials which are generally formed via coordination bonds between metal ions or clusters and organic linkers. Although they already have wide applications, their combination with other functional materials results in the formation of new multi-functional hybrid materials with combined or synergistic properties of the individual components. These new nanohybrid materials with novel properties expand the applications of metal organic frame works.

Here, I summarized the research on the electrosynthesis of MOFs and introduce a new method to synthesize thin films of the well-known metal organic framework ZIF-8 on zinc oxide nanorods. Zinc oxide nanorods are synthesized electrochemically on FTO substrates. A 2-methyl imidazole solution was then casted on these zinc oxide nanorods. Casting a thin film of the linker solution on the zinc oxide nanorods allows the underlying morphology to be preserved, leading to the facile and precise formation of nanostructured hybrid materials under short reactions times and conventional heating. This method allows for the fast and facile formation of nanostructured metal organic framework-semicondoctor nanohybrid thin films with minimum use of both solvents and linker. We also present the effect of various synthesis parameters on the morphology of the resulting thin film, and the role of solvent.

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T05. **Interactions of drugs and lipidic drug carriers with model lipid membranes prepared by Langmuir-Blodgett-Shaefer technique**

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The lipidic cubic phase is a bicontinuous mesophase consisting of two sets of noncommunicating but interpenetrating water channels confined in-between lipid bilayers. It resembles a molecular sponge allowing to host significantly larger amounts of drugs, compared to other carriers e.g. liposomes or gold nanoparticles. Holding the drug inside the cubic phase or cubosome nanoparticle may decrease its toxic effects towards healthy cells while appropriate mechanisms can stimulate the release of the drug from the carrier when it approaches e.g. the cancer cell environment (1, 2). Drug diffusion and kinetics of release from the mesophase depend among other factors on the nanostructure and aqueous channels sizes of the cubic phase which are defined by the amphiphilic molecules used for the formation of the mesophase. We present the electrochemical studies of drug transport and sustained drug release from lyotropic cubic phases and cubosomes. Using chronocoulometry and voltammetry at micro and normal – size electrodes we show the dependence of diffusion of an electroactive drug on the size of the channels and on pH (2, 3).

To utilize the cubic phases gels and cubosomes in drug delivery, one has to understand their interfacial properties at biological interfaces. Therefore we prepared a model membrane – monolayer of lipid at the air-water interface. It corresponds to one leaflet of the biological membrane. We studied the behaviour of anticancer drug – doxorubicin and of cubosomes – carrying the drug in contact with the lipid layer. The mechanism of cubosome internalization and its effect upon the fluidity and permeability of the membranes are discussed.

Langmuir monolayer studies revealed that both the drug and the cubosome incorporate into the biomimetic layers more easily from the buffer of pH = 7.4, than from the buffer, pH 5.4 This difference is important since the environment of cancer cells is more acidic than that of normal cells. The changes in the membrane organization were reflected in the increase of area per molecule and decrease in compression modulus of the lipid membrane and were seen also in Brewster Angle Microscopy images. The incorporation of the drug into biomimetic membranes was confirmed by electrochemical studies performed for supported monolayers transferred from the subphase containing the drug. The proposed mechanism of the drug incorporation into the layers will be presented.

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K06. **Label and Label-free Electrochemical biosensing platforms for microRNA detection**

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Discovered only in 1993, in the soil nematode *Caenorhabditis elegans*, microRNAs (miRNAs, miRs) are nowadays considered powerful and paradigmatic diagnostic and prognostic clinical biomarker candidates for many human diseases. These include a broad range of cancers, heart diseases, immunological and neurological diseases. In particular, regarding cancer, miRNA profiles not only distinguish between normal and cancerous tissues and identify tissues of origin, but they can also discriminate between different subtypes of a particular cancer, even specific oncogenic abnormalities. Recently, the awareness of the presence of miRNAs not only within cells but also in body fluids, paves the way for noninvasive biomarker analysis. Furthermore, since deregulated miRNA expression is an early event in patients with cancer, measuring circulating miRNA levels, may also be useful for early diagnosis, obtaining high advantages to the success of the treatment.

Actually, there are several techniques for the detection of miRNAs (like miRNA microarrays, quantitative Real-Time PCR (qRT-PCR) and next-generation sequencing) each of them with their own unique advantages and disadvantages. However, most of these approaches are not compatible with Point-Of-Care Testing (POCT). A great deal of effort has been devoted to develop new compact analytical methods for miRNA decentralized analyses that possess appropriate sensitivity and multiplexing capability without PCR. In this instance, electrochemical genosensors have emerged as particularly attractive options for miRNA detection in terms of simplicity of use, assay time and amount of sample required.

In this paper, we reported the development of a label-free impedimetric genosensor for miRNA detection, using a miniaturized, polymer-modified sensor. In particular, a polymer bearing an intact biotin moiety available for streptavidin binding was used. This fact gave rise to the ability to nanostructure the sensor surface increasing the capture probe immobilization efficiency in terms of orientation, loading and steric hydrance.

Moreover, in a further approach, faradic impedance spectroscopy has been used coupled to an enzymatic amplification of the hybridization event. Basically, DNA capture probes are immobilized onto electrode surfaces. Total RNA is extracted from the sample, biotinylated, and then hybridized with the specific capture probes. The biosensing platform is then incubated with streptavidin alkaline phosphatase and exposed to a proper substrate. The product of the enzymatic reaction is electrochemically monitored. Biotin labeled liposomes, have been also tested as a functional tether for the enzyme molecules.

Both the label-free and label-based approaches allow the detection of miRNAs in cancer cells and the results are herein reported.

T06. **Nanoparticle Imprinted Polymers**

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The expected broad utilisation of nanoparticles (NPs) calls for a detailed consideration of their specific toxicological effects and monitoring their release into the environment (nanotoxicology).[1] Appropriate in vitro sensing tools should provide information about the possible interaction between nanoobjects (characterized by core material, size, shell chemistry and shape) and biological systems. Recently, we published a new concept based on nanoparticle-imprinted polymers (NIPs, Figure 1) combined with electrochemical detection.[2] It was first demonstrated with a polyaniline film transferred simultaneously with template AuNPs by the Langmuir-Blodgett technique.

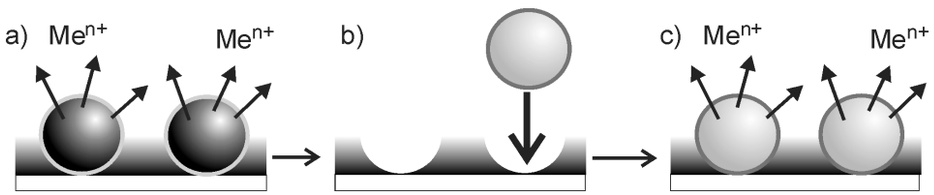

Figure 1: NP detection with NIPs. a) electrochemical removal of template NPs; b) reuptake of analyte AuNPs into nano voids; c) detection of analyte NP.

In order to extend this concept, new ways are sought to build the matrix from low molecular building blocks. After binding AuNPs as templates to a 3-aminopropyltriethoxysilan (APTES)-modified indium tin oxide (ITO) electrode, a polymer matrix is generated either by electropolymerisation of self-inhibiting poly(phenol) and poly(plumbagin)[3] films or by spin-coating an ultrathin poly(dimethylsiloxane) (PDMS) layer.[4] SFM images proved the presence of templates within smooth, 5 to 20 nm thick matrices. Template NPs were chemically removed in potassium cyanide, leaving their shape and size imprinted in the polymer as evidenced by different techniques like SEM and Pulsed Force Microscopy (PFM). The recognition ability and size selectivity of NIPs was investigated by immersing the matrix in aqueous solutions containing citrate-capped AgNPs. The presence of analyte AgNPs was verified electrochemically in an aqueous $NaNO_3$ solution as by LSV. Complementing studies by UV-Vis and X-ray photoelectron spectroscopies corroborated the template embedding, template release and analyte NP uptake.

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SC04. **Carbon nanotubes supported *Escherichia coli* for electrocatalysis of volatile organic compounds**

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Toxic volatile organic compounds (VOC) originating from chemical and electronics industries present a challenge to receiving environments and wastewater treatment processes. Rapid VOC detection is part of wastewater quality monitoring process.[1,2] Mass spectrometry[3] and chromatography[4] based VOCs sensors are too expensive for distributed applications, thus high-performance low-cost VOCs sensors are needed. Here, we propose a novel electrochemical VOCs sensor based on *Escherichia coli* bacterial cells attached on carbon nanotube (CNT)-coated screen printed electrode (SPE). CNT-SPE has a higher current output than conventional graphite SPE, because of the CNT high specific active surface. Moreover, CNT interface favors attachment of electrochemically active microorganisms (EAM) due to the high content of oxygen-containing functional groups (C-OH, C=O, etc.) present on its surface. The proposed sensor assembly is used for detection of selected VOCs in wastewater. The sensitivity and detection limit towards 1-cyclohexyl-2-pyrrolidone (CHP) were of 1.6 nA ppm^{-1}, and ~10 ppm, respectively. Other sVOC commonly found in wastewater like dimethylacetamine (DMA), methylbenzene (MB), cyclopentanone (CPN), and dibutyl phthalate (DBP) did not interfere with CHP determination. To the best of our knowledge, this is the first report on bioelectrochemical detection of VOCs. This work offers a straightforward route to enhance the detection of organic contaminants for environmental applications.

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T07. **Graphene Surface Decorated with Biomimetic Donor-Acceptor Dyads for Modulating of Electron Transfer Dynamics**

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Graphene, an all carbon atom hexagonally arranged in a planar condensed ring system of quasi infinite size, has become a rising star within the family of carbon nanomaterials in recent years. This one atom thick material known for its extraordinary strength, high flexibility, optical transparency, elasticity, and unique electrical and optical properties has made researchers seeks immediate applications in the areas of flexible sensor arrays and optoelectronic devices.

Sequential electron transfer or electron transfer/hole transfer between energetically well-positioned entities of photosynthetic reaction center donor-acceptor models is one of the commonly employed mechanisms to generate long-lived charge separated states. Wealth of information, applicable towards light energy harvesting and building optoelectronic devices, has been acquired from such studies. The focus of this talk is to highlight our recent progress in the design, construction and electron transfer properties of tetrapyrrole-nanocarbon graphene hybrids. The self-assembly methods developed to build the tetrapyrrole-nanocarbon graphene hybrids involving p-p stacking with the help of suitably functionalized tetrapyrrole and graphene materials will be discussed. Photoinduced electron transfer leading charge separation in the nanohybrids will be emphasized. Finally, the advantages and limitations of the present tetrapyrrole-nanocarbon hybrids in light-to-electricity conversion schemes will be highlighted.

K07. **Molecular engineering; nanoscale surface design of biosensors, and smart nanoparticles.**

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Biosensors, functional nanoparticles and nanofibres all depend on immobilisation of biological molecules (antibodies, binding proteins, enzymes and others) onto the surface substrate. Performance is critically affected by the nature of the organic base layer onto which the biomolecules themselves are tethered, their orientation and surface loading. In addition, the surface chemistry of the base layer is also important in minimizing non-specific interactions which tends to elevate the background signal and thereby raise the limit of detection.

For affinity biosensors then antibody orientation can be achieved by a variety of routes, using either biotin/avidin mediated coupling or by direct crosslinking with heterobifunctional crosslinkers. For whole antibodies (IgG) use can be made of the oligoglycans on Fc; periodate oxidation followed by linkage of amino biotin the aldehyde created, coupled with NHS biotin mediated modification of the base layer allows the oriented display of IgG. Alternatively, mild reductive cleavage of IgG creates half antibodies with two unique and close Cys –SH groups which can be utilised for amine to thiol mediated crosslinking, e.g. with sSMCC.

For the muscle damage/heart attack marker myoglobin, then oriented antibody attachment raises the detection limit by at least 1-2 orders of magnitude. For smaller binding reagents, including camelid nanobodies and purely artificial binding proteins such as the Adhirons, they can be engineered to possess a terminal Cys. In addition, their height above the electrode surface, so as to position them optimally within the Debye layer, critically affects the amplitude and type of impedance change occurring upon analyte binding.

With particulate (nano)biosensors then again orientation and surface chemistry are also important. In fluor-loaded nanoparticles targeted against CEA, a biomarker for colorectal cancer (CoRC) then correct attachment to the particle surface is needed to provide correct particle targeting. The optimum attachment protocol, using an amino-tagged PAMAM dendrimeric linker provides correct targeting to CoRC cells in culture or CoRC *in vivo*, with minimal nonspecific binding. These parameters will be discussed with reference to antibody, enzyme and Adhiron based affinity biosensors for a range of biological analytes and antibody targeted nanoparticles for *in vivo* cancer imaging.

SC05. **Metallic nanostructures for virus detection and determination**

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Viruses are small infectious agents which cause various diseases like hepatitis, mononucleosis, influenza or pneumonia. In order to apply appropriate and effective therapies quick and proper identification of the virus is needed. Both in practice and literature there are many methods known for detection of viruses, eg. Enzyme-Linked ImmunoSorbent Assays, microscopy techniques like Surface Plasmon Resonance or Raman spectroscopy. Despite the many available techniques, false positive or negative test results are still often given. Hence the need to seek new solutions.

In this work metallic nanostructures were used for detection of bacterial virus. The bacteriophage T7 was used as a model system of mammalian viruses belonging to the family of adenoviruses. In the first approach, gold nanoparticles were modified with antibodies [1] or a polymer [2] and the changes of the localized surface plasmonic resonance band were observed caused by immunocomplex formation. This results in sensitive and fast immunotests with a detection limit in the pM [1] or fM [2] range.

In the second approach silver nanowires were used to immobilise the antibodies. Then a combination of transmission imaging of the metallic nanostructures with fluorescence microscopy was applied to verify the immunocomplex formation.

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K08. **Membrane-modified electrodes for the study of proton-pumping enzymes and membrane-bound hydrogenases**

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Bioelectrochemistry has been extremely valuable in elucidating the catalytic mechanism of respiratory redox enzymes, although in almost all cases only globular enzymes or water-soluble subcomplexes have been investigated. In biology, however, many respiratory reactions are catalysed by redox enzymes that reside in the lipid membrane, where they play a major role in almost all metabolic processes, including photosynthesis and biochemical processes such as the nitrogen cycle. The relative lack of bioelectrochemical studies of membrane proteins are due to their amphiphilic nature, which make them difficult to handle experimentally, especially in sensitive electrochemical experiments where proteins are prone to denaturation on the electrode surface.

By modifying ultra-flat electrode surfaces with so-called tethered bilayer lipid membranes (tBLMs) or intact vesicles, supramolecular platforms can be constructed that enable the electrochemical characterisation of membrane-bound redox enzymes contained within these membrane-modified electrodes. In this presentation, two examples will be discussed in which membrane-modified electrodes have elucidated respiratory processes.

In the first example, a membrane-bound [NiFe]-hydrogenases (MBH), which has been extensively studied for applications in hydrogen−oxygen fuel cells, was incorporated in a tBLM. The MBH of *Ralstonia eutropha* was used in this study as compared to other MBHs it is relatively insensitive to deactivation by oxygen. Previous bioelectrochemical studies with the water soluble subcomplex of MBH, lacking the membrane-bound subunit, showed that this MBH is inactivated at high potentials, especially in the presence of oxygen. In contrast, cyclic voltammetry and chronoamperometry experiments show that MBH, when in equilibrium with the quinone pool in the tBLM, does not inactivate under oxidative redox conditions. Furthermore, although the MBH in the tBLM is still inactivated by O_2, reactivation was found to be fast even under oxidative redox conditions. We propose that this enhanced resistance to inactivation is due to the fact that MBH is in a more native-like environment in the tBLM.

In the second example, a heme-copper oxidase (HCO) is incorporated in intact vesicles on the electrode surface to create a single-enzyme platform that monitors proton pumping by this enzyme. This a single-enzyme study reveals that cytochrome bo_3 from *Escherichia coli*, an HCO closely homologous to Complex IV in human mitochondria, can enter a rare, long-lifetime leak state during which proton flow is reversed. The probability of entering the leak state is increased at higher transmembrane pH gradients. By rapidly dissipating the PMF, we propose that this leak state may enable cytochrome bo_3, and possibly other HCOs, to maintain a suitable pH gradient under extreme redox conditions.

K09. **Heated Electrochemical DNA Sensors for Molecular Diagnosis of Genetic Defects and Infectious Diseases**

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DNA capture probes were immobilized on various gold electrodes via dithiol-linkers. The target strands were covalently modified on either their 5'- or 3'-end with osmium tetroxide bipyridine labels at five terminal thymine bases using protective strands to preserve the recognition site (1). After using this approach for melting curve analysis of DNA mismatches (2), we have also reported on analysis of genetically modified maize in real flour samples (3). Recently, we measured very high activation energies (up to 200 kJ/mol) for the displacement of protective DNA strands by the surface-confined capture probes (4). This was observed with both gold disk electrodes in a heated bulk solution and heated gold wires in cold bulk solution.

This paper reports about extremely different sequence-dependent hybridization behavior of fully complementary and single-base-mismatched DNA targets influenced by the hybridization temperature. We have compared 4 different DNA sequences designed to detect single nucleotide polymorphisms (SNPs) relevant for autoimmune diseases. We expected that fully complementary targets would deliver higher signals than mismatched target strands. We found dramatic influence of both the target sequence and location of the osmium tetroxide labels. Our results suggest that labels located in close proximity to the gold surface have a greater tendency to behave as expected. Furthermore, distal labels (at the opposite end of the double strand) can yield unexpectedly high signals affected by the presence of mismatches. As a possible explanation, we consider most DNA strands to lay flat on the electrode surface with many of them resting on each other. This behavior could be used for molecular diagnosis of genetic predispositions based on SNPs.

Another clinical application is biosensors that can detect infectious fungi. We have obtained preliminary results with *aspergillus fumigatus*. Similarly to maize detection (3), we have performed PCR coupled with electrochemical product detection. In the latest study, however, the osmium tetroxide labeling was integrated into the denaturation procedure of the fully double-stranded PCR products.

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2015-11-08, Sunday

08:00 – 09:00 Breakfast

09:00 – 10:30 **Morning Session 1**
(chairs: Sergey Shleev, Nikolaos N. Daskalakis)

09:0 – 09:40	T08	**Sergey Shleev** Electric power biodevices
09:40 – 10:00	K10	**Nikolaos N. Daskalakis** Quantitative lateral flow assay for monitoring of kidney disease
10:00 – 10:15	SC06	**Piotr Warszynski** Multifunctional hybrid ultrathin polyelectrolyte coatings
10:15 – 10:30	SC07	**Paweł Weronski** Application of rotating disk electrode technique in studies of supported thin films of spherical particles

10:30 – 11:00 Coffee Break

11:00 – 12:55 **Morning Session 2**
(chairs: Izabella Brand, Bozena Sikora)

11:00 – 11:40	T09	**Bozena Sikora** Opto-magnetic nanoparticles for biological applications
11:40 – 12:00	K11	**Lubomir Svorc** A state-of-the-art on chemical modification of boron-doped diamond electrodes for applications to biosensors and biosensing
12:00 – 12:20	K12	**Izabella Brand** In situ detection of molecular scale changes induced in model membranes due to lipid – protein interactions
12:20 – 12:35	SC08	**Stanislav Trashin** Attaching of redox proteins on electrodes by “gluing” with oligosilanes for direct electron transfer
12:35 – 12:55	K13	**Sarah Horswell** Electrochemical and infrared studies of phospholipid bilayers supported on Au(111) surfaces

13:00 – 14:00 Lunch

14:30 – 16:10 **Afternoon Session 1**
(chairs: Ambra Giannetti, Karsten Haupt)

14:30 – 15:10	T10	**Karsten Haupt** Molecularly imprinted polymer nanogels and nanocomposites as plastic antibody mimics for bioimaging and theranostics
15:10 – 15:50	T11	**Ambra Giannetti** Fluorescence based optical biosensors
15:50 – 16:10	K13b	**Patrizia Mussini** Inherently chiral electrodes, the effective tool for chiral voltammetry

17:00 – 20:00 Castle exploration with treasure hunting

21:30 – 23:00 Dinner/Banquet

T08. **Electric power biodevices**

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The lecture will overview the critical advances in electric power biodevice technology. Electric power devices that employ biocatalysts can be classified as biological electric power sources (1). Generally accepted and novel classifications of biological electric power devices, such as conventional biofuel cells and biobatteries, charge-storing biofuel cells and self-charging biosupercapacitors, will be presented and exemplified based on the comprehensive literature analysis (2-4). During the lecture significant attention will be also devoted to proper surface modification procedures to design modern biomaterials serving as positive and negative electrodes of high-performance, stable, and efficient electric power biodevices. Possibility to use biological power sources as self-powered electrochemical biosensors will be also highlighted (5-7).

Acknowledgements

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K10. **Quantitative lateral flow assay for monitoring of kidney disease**

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Chronic kidney disease (CKD) is a condition where the kidney's ability in filtering waste products from the blood is impaired. It has a devastating impact on people's quality of life and is a major challenge for health systems worldwide with rates of CKD reported to be increasing globally.

In England alone, 1.8 million people are diagnosed with CKD, while an additional 1 million cases remain undiagnosed and thus untreated. CKD costs the English health services in excess of £1.4 billion per annum, which is more than breast, lung, colon and skin cancer combined.

There is currently no device that can be used by patients or clinicians for near patient quantitative monitoring of kidney function; existing methods for point-of-care testing are semi-quantitative and clinicians rely on laboratory testing for assessment and monitoring. We are developing a novel biosensing platform for quantitative diagnosis and monitoring of kidney function at the point of care. This combines the simplicity, low cost and speed of readout of lateral flow immunoassay with the sensitivity and quantitation of electrochemical detection. The digital readout of the test enables the automatic and accurate collation of kidney function readings into a central database using mobile technology.

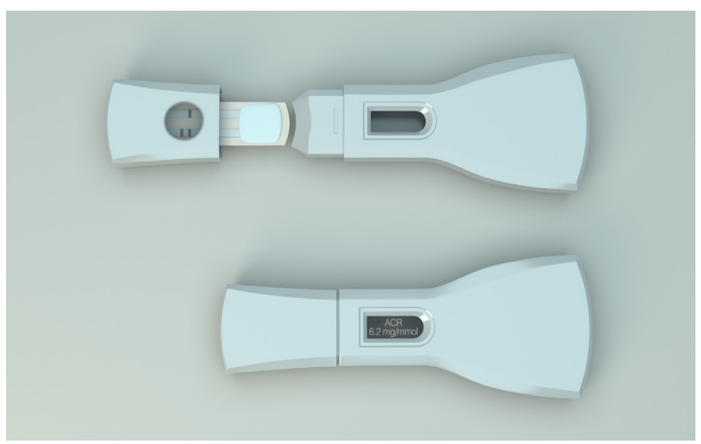

Figure 1. Artist rendering of the device with the disposable strip inserted into the reader

SC06. **Multifunctional hybrid ultrathin polyelectrolyte coatings**

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Sequential adsorption of charged nanoobjects, as polyelectrolytes or nanoparticles, known also as the "Layer by layer" (LbL) deposition method, is considered as one of the most promising techniques of surface modification and formation of highly tailored functional thin films for a wide range of possible applications, including: selective membranes, biosensors and drug delivery systems.

One of the most significant problem for sensors in contact with biological fluids is the process of biofouling, i.e. the unwanted adsorption of proteins, occurring on the surfaces exposed to solutions containing biological material. Therefore, the development of the "antifouling" coatings protecting against non-specific protein adsorption, bacteria and fungi colonization is an important area of the research within a broader field of biointerface science.

One goal of this work was to build up anti adhesive films able to cover any type of surface. These films are expected to reduce/eliminate the non-specific adsorption of proteins at surface as well as the bacterial colonization of implanted materials. We used synthesized copolymers of poly(glutamic acid) or poly(L-lysine) with grafted PEG chains with various grafting ratio and various chain lengths for formation of the external layer of multilayer films. The biofouling process was investigated by studying the adsorption of different proteins: HSA, fibrinogen as well as proteins from Human serum using QCM.

Our second goal was to use graphene - a new material consisting of single layer of sp^2 – bonded carbon atoms with unique two-dimensional (2D) nanostructure of a honeycomb lattice as a component for film formation. As graphene is a hydrophobic, it can not be directly used for construction of multilayer films with the LbL method. Therefore, we proposed to use suspension of graphene oxide (GO) for formation of such films and its subsequent reduction to the reduced graphene oxide (rGO). We demonstrated that using the proposed method it is possible to obtain ultrathin conductive films on quartz and polyimide (PI) plates. We also constructed by the LbL method the sensor layers containing rGO and Prussian blue nanoparticles. We observed that the intensity of the redox current of PB embedded in the multilayer films markedly increased due to enhancement of electron transport to the modified polyimide electrode surface. In the presence of hydrogen peroxide characteristic peaks from reduction of H_2O_2 to OH^- ions and oxidation to O_2 molecules appeared. Formation of such thin films on PI allows creating flexible electrodes, which can find applications in biomedicine as disposable, electroactive sensors. Our results show that by the LbL method the electrochemical sensors protected by the antifouling layer can be constructed.

SC07. **Application of Rotating Disk Electrode Technique in Studies of Supported Thin Films of Spherical Particles**

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Adsorption of colloidal particles at solid/liquid interfaces is a common natural phenomenon, which has many applications in medicine and industry. The accumulation of particles can lead to a spontaneous formation of mono- or multilayer structures of the thickness of the order of micrometer. Quantitative characterization of such multilayers is a non-trivial task. A non-invasive technique providing means to study the layers in wet conditions is that of rotating disk electrode.[1,2] We have presented a short review of our recent research on the application of this technique in studies of diffusion in layers of spherical particles. We have discussed our theoretical model for the description of adsorbed particle-monolayer effect on the limiting diffusion current at a rotating disk electrode.[3] We have demonstrated that electrochemical measurements of the limiting diffusion current at a rotating disk electrode with a monolayer of adsorbed particles provide means for the determination of the electrode surface coverage. Then, we have verified our predictions experimentally and determined the application range of our theoretical model.[3,4] We have also presented results of our theoretical and experimental research on multilayers of spherical particles assembled layer by layer. We have used a Monte Carlo model[5,6] to create a number of virtual multilayers of hard spheres at a solid-liquid interface, at various surface coverages and numbers of single layers. For each of the multilayers, we have determined its mean thickness, porosity, tortuosity, and equivalent thickness of stagnant solution layer.[7] From our simulation results, we have determined the equivalent layer thickness as a function of the mean surface coverage and layer number of multilayer. We have also tested our theoretical results experimentally.[8] We have found a good agreement between the numerical simulations and experiments. We have also demonstrated that our approach provides means to study the kinetics of colloidal particle adsorption at the rotating disk electrode. With the novel method, we can estimate the surface-charge heterogeneity of colloidal particle as well.

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T09. **Opto-magnetic nanoparticles for biomedical applications**

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Multifunctional nanoconstructs based on rare earth ions-doped β-$NaYF_4$ up-conversion nanoparticles (UCNPs) and superparamagnetic Fe_3O_4 nanoparticles (SPIONs) co-encapsulated in SiO_2 were synthesized and characterized. These nanoconstructs revealed simultaneously unique photo-luminescent and magnetic properties. In particular, UCNPs&SPIONs@SiO_2 combine the capability of up-conversion of near-infrared into visible light with superparamagnetic properties. The nanoparticles can be applied to image pathological tissues and for the *in-situ* generation of reactive oxygen species (ROS). Additionally, superparamagnetic properties of UCNPs&SPIONs@SiO_2 offer numerous advantageous functionalities, including: nanoparticle-tracking with an external magnetic field gradient, enhanced contrast in magnetic resonance imaging, as well as diseased tissue eradication *via* local heating with alternating magnetic field (hyperthermia).

Prior to obtaining UCNPs&SPIONs@SiO_2 (by co-encapsulation), UCNPs with sizes < 20 nm and high efficiency of up-conversion luminescence (UCL), were synthesized by co-precipitation. The whole palette of UCL emission bands, resulting from the presence of various rare earth ions, was obtained. Moreover, under NIR light stimulation, the UCL

of thus obtained UCNPs could excite molecules of a well-established photosensitizer, Rose Bengal, towards an efficient ROS generation.Toxicity remains one of the fundamental issues concerning biological and medical application of advanced materials. Therefore, we tested our materials in living HeLa, HEK293 and astrocytes cells with using commercial viability tests, i.e. MTT and Presto Blue assays. We showed that the opto-magnetic nanoconstructs are relatively non-toxic thus they are potentially useful for the selected medical application.

Acknowledgements: The research was partially supported by the EU within European Regional Development Fund, through the grant Innovative Economy (POIG.01.01.02-00-008/08), the project „Development of the cluster center of biomedical engineering" implemented under Economy Operational Program (project no. UDA-POIG.05.01.00-00), the grants of PNSC 2013/11/B/NZ1/00089, NN UMO-2013/08/A/ST3/00297, DEC-2012/07/B/ST5/02080 and DEC-2014/15/D/ST5/02604. This work has been done in the NanoFun laboratories co-financed by the European Regional Development Fund within the Innovation Economy Operational Program, the Project No. POIG.02.02.00-00-025/09/. This research was also co-financed by the Swiss National Science Foundation through the Nano-Tera.ch Focused Project (NTF), 'NanoUp'.

K11. **A state-of-the-art on chemical modification of boron-doped diamond electrodes for applications to biosensors**

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The performance of electrochemical biosensors generally depends on the nature of the transducer and the methods used for the immobilization of biorecognition element. Various conventional electrode materials such as metals, graphite, glassy carbon, gold, etc., have been widely employed as transducers in development of biosensors due to simple preparation and suitability for chemical modification. However, their primary drawbacks consist in long-term instability, low reproducibility, inhomogeneity of related biointerfaces and higher background current. Hence, strategies for development of novel materials for further surface functionalization using controllable biomolecule immobilization are recently still of importance. Boron-doped diamond (BDD) has received growing interest owing to its wide potential window, low background current, biocompatibility, good chemical stability in comparison with conventional materials[1]. However, it should be taken into consideration that these properties are dependent on dopant concentration, surface termination, non-diamond carbon content and grain boundaries. By tuning these parameters, the BDD functionalization efficiency could be controlled to construct effective and reliable electrochemical biosensors.

The present state of the art clearly shows that it is still necessary to develop novel sophisticated approaches for chemical modification to construct innovative, fast, sensitive and reliable electrochemical biosensors[2]. In the respect of above mentioned facts, the objective of this contribution is to introduce advanced strategies for design of electrochemical biosensors using BDD electrode as novel transducer. Different ways and steps of the chemical modification of this electrode will be demonstrated. For instance, the effect of different doping levels of BDD on the surface functionalization for DNA assays by means of electrochemical reduction of aryldiazonium salts will also be discussed[3].

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K12. *In situ* detection of molecular scale changes induced in model membranes due to lipid – protein interactions

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Lipid molecules build a fluid matrix of biological membranes which host a large number of proteins and constantly experience interactions with them. Proteins associated with membranes have developed various ways of interactions with lipid molecules. They appear either as nonspecific interactions or specific interactions of a variable strength. The following specific interactions occur between proteins and lipids in the membrane: binding to a polar moiety at a lipid head group, electrostatic interactions with polar head groups of lipids, anchoring of a hydrophilic fragment of a protein into the membrane, insertion of a fragment of a lipid molecule into the protein, insertion of a protein into the membrane and aggregation of monomers of transmembrane proteins into the membrane. Clearly, these interactions influence the macroscopic and microscopic properties of biological membranes such as the permeability to ions, capacitance, lateral composition, orientation and physical state of lipid molecules as well as the activity and structure of proteins. In addition, static electric fields in the order of $10^7 – 10^9$ V m^{-1} constitute to the natural environment of lipids and proteins present in biological membranes. Under these conditions the structure, orientation and hydration of biomolecules may differ from that in the bulk phase.

In situ studies of changes in models of biological membranes due to the lipid-protein interactions bring a need of use bioanalytical methods which would allow for carrying out sensitive, selective, reproducible, measurements of the composition and function of these complex biological systems. The deposition of biomimetic films on electrode surfaces allows studies of the electric-field driven changes in these assemblies. Electrochemical techniques, however, are not sensitive to the structure of molecules adsorbed on the electrode surface. The determination of the structure of molecules adsorbed on electrode surfaces requires a use of spectroscopic and/or microscopic methods combined to electrochemical techniques. Infrared spectroscopy (IRS) gives the unique opportunity to analyse simultaneously each kind of species present in an assembly adsorbed at the electrode surface. In contrast to other spectroscopic techniques, a complex composition of a film limits neither the spectroscopic resolution nor sensitivity. Since various functional groups present at various molecules absorb the infrared light at specific frequencies, the influence of each component on the structure of the entire assembly can be studied simultaneously without labelling with any molecular probes. The reflection-based IRS techniques such as the polarization modulation infrared reflection-absorption spectroscopy (PM IRRSA) have been successfully applied to the analysis of the electrode|electrolyte interface.

In this paper the impact of the interaction of two proteins: glycoprotein (siglec) and anchoring protein (recoverin) on the structure and orientation and electrochemical properties of lipid and protein molecules in models of biological cell membranes will be presented.

SC08. **Attaching of redox proteins on electrodes by "gluing" with oligosilanes for direct electron transfer**

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Immobilization of redox proteins on electrode surface is a powerful method for electrochemical studies of redox proteins as well as developing biosensors and biofuel cells based on direct bioelectrocatalysis. Simple adsorption of proteins on electrode surface is often failed because of desorption and denaturation. Strategies related to cross-linking, covalent chemisorption and entrapment in polyelectrolytes are harmful for native state of proteins and often allow only limited potential window. Thus, an universal strategy of choice, which would suggest an electrochemically inert and stable surface and gentle attaching of proteins, is not clear.

We suggest oligosilanes polymerized in-situ from a monomer water solution mixed with a protein and dried on an inert electrode as universal immobilization strategy for redox proteins. This gentle way of immobilization was tested with three heme-containing redox proteins (horse heart Cytochrome C with E0' = 0.04 V, globin-12 from C. elegans[1] with E0' = −0.23 V and human neuroglobin (NGB)[2] with E0' = −0.37 V vs. SCE) and provided a direct electron transfer between the proteins and the electrode. In all cases the surface coverage was close to a monolayer, and surface kinetic constant k_s exceeded 50 s^{-1} giving only slight redox peak separation at scan rates up to 2 Vs^{-1}. Control without oligosilane showed minor or no redox peaks because of fast dissolving of the pre-adsorbed proteins in bulk buffer.

The proposed immobilization method can be applied for studding redox and catalytic properties of enzymes. Particularly, we monitored interaction of NGB with oxygen and further with nitric oxide (NO). In the presence of oxygen the peak current for reduction of ferric NGB was suppressed and the peak of oxidation of the ferrous NGB disappeared because of oxygen binding with the ferrous NGB. When NO was injected in the cell, peaks of oxidation/reduction of NGB were recovered due to interaction of NO and ferrous NGB-O2 complex with release of ferric NGB. Strong effect of NO on the peak current of the immobilized neuroglobin allows to measure NO at concentrations 0.1–1.0 μM by a potentiodynamic mode (DPV or SWVA) at low potentials. The use of natural biological element (NGB) for monitoring NO through measuring the redox state of the protein is closely related to the biological function of NGB and might be relevant for monitoring NO in the cells of natural occurrence of NGB (i.e. nervous and endocrine tissues, cerebrospinal fluid and retina).

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K13. **Electrochemical and Infrared Studies of Phospholipid Bilayers Supported on Au(111) Surfaces**

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The structure of phospholipid bilayers supported on surfaces is of widespread interest, as they provide a natural environment for the immobilisation of proteins (such as antibodies, membrane functional proteins and hormone receptors) on solid surfaces in natural conditions. This allows both the study of the function of proteins and the functionalisation of solids to produce sensing devices based on optical or electrical detection of ligand binding.(1) To investigate these fully, it is necessary first to study the supporting matrix; *i.e.*, the lipid bilayers.(2) Most studies of an applied nature use "representative" lipids or lipid mixtures as model biomembranes and, whilst electrochemists have studied electrochemical phase transitions of lipids of differing structure,(1b) it has only been relatively recently that the structures of lipid bilayers themselves, in the presence of applied electric fields, have received much attention.(2,3) By supporting the lipid bilayers on electrode surfaces, we have the means to apply an continuously tunable electric field, comparable with those found in nature (~10^7 - 10^8 V m^{-1}),(3) through varying the applied potential and thus controlling the charge. A range of *in situ* structural probes is available to determine bilayer structure at the molecular level, under potential control, including vibrational spectroscopy, imaging techniques and neutron reflectivity.(3c)

In this presentation, we shall discuss how the size and shape of molecules affects their organisation within bilayers and how they respond to the applied electric field. Dimyristoyl phosphatidyl ethanolamine (DMPE) exhibits very tight packing as a result of its cylindrical shape and intermolecular hydrogen bonding interactions. These factors lead to the formation of a bilayer that has low capacitance and little responsiveness to the electric field.(2b) Dimyristoyl phosphatidyl serine (DMPS), although of similar size, is charged and this leads to quite different bilayer structure and properties.(2c) We shall show how doping a small quantity of DMPS into a DMPE bilayer can give rise to distinct changes in the DMPE bilayers, rendering them more responsive to the applied field but without altering adversely the electrical barrier properties. These findings could help to explain why only low levels of anionic lipids are found in natural cell membranes. They also have implications for sensing because they suggest that it is feasible to generate lipid films with both favourable barrier properties and the flexibility to accommodate structural changes in embedded functional molecules, which would be important in the design of sensing devices.

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T10. **Molecularly imprinted polymer nanogels and nanocomposites as plastic antibody mimics for bioimaging and theranostics**

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Molecularly imprinted polymers (MIPs) are synthetic antibody mimics ('plastic antibodies') that specifically recognize molecular targets.[1,2] They are highly cross-linked polymers that are synthesized through the polymerization of monomers bearing suitable functional groups, in the presence of the target molecule acting as a molecular template. This templating induces three-dimensional binding sites in the polymer that are complementary to the template in terms of size, shape and chemical functionality. Thus, the plastic antibody can recognize and bind its target with an affinity and selectivity similar to a biological antibody.

We present here a new approach allowing for the synthesis of MIP by controlled/living radical polymerization using a dendritic multiiniferter.[3] This results in protein-size, soluble MIP nanogels with a homogeneous size distribution. Their mean diameter is 17 nm and the average molecular weight 97 kDa, thus their size and density are very close to those of biological antibodies. The MIP nanogels show specific binding of their targets, small organic molecules or proteins, with a nanomolar affinity and a good selectivity. We also present new methods to prepare MIPs specific for proteins based on solid-phase synthesis around the immobilised template,[4] In addition, the direct coating of thin MIP films around functional inorganic cores such as magnetic nanoparticles,[5] gold nanoparticles,[6] upconverting nanoparticles,[7] by controlled and localized photopolymerization[5,7,9] will be described.

The use of these functional nanomaterials for biosensing,[6] as well as for cell and tissue imaging[8] will be discussed.

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T11. **Fluorescent-based optical biosensors**

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Optical sensors and biosensors are part of a growing research area including spectroscopy (absorption, luminescence, Raman scattering) and refractometry (surface plasmon resonance, interferometry, optical resonance) based systems.
Experts in the field, who have highlighted the advantages of optical sensing over other transduction methods, have published a wide range of books and review articles on this subject in the last decades. Fluorescence is by far the method most often applied and comes in a variety of schemes [1], which can be applied to industry, environmental monitoring, medicine, biomedicine and chemical analysis.
Health-care is the application field which is presented in this work, not only considering their possible invasive applications (the high degree of miniaturisation of optical fibre sensors, their considerable geometrical versatility, and extreme handiness make it possible to perform a continuous monitoring of numerous parameters, thus enabling performances which are often unique) but also taking into account the development of optical multiarray biochips for the analysis of multiple parameters, essential in view of an immediate rapid screening of the patient pathology.
The sensors for medical diagnostics can be classified in three main classes: i) invasive sensors, where the sensor enter the human body using suitable catheters/tubing [2]; ii) minimally invasive sensors, which limit their contact with the human body, for example to the tissue [3], and iii) not invasive sensors, where the device has no contact with the human body and the measurement is performed on biological samples drawn from the patient [4].
In recent years, the importance of optics in the biomedical area has been increasing owing to the advent of nanophotonics, which is opening completely new perspectives. Thanks to the reduction of the probe size to nanoparticles, optical nanosensors have been developed, which penetrate the cell membrane and measure chemical and biochemical analytes directly inside the cell [5].
The fundamental basis of chemical and biochemical fluorescence sensing are summarised and the new trends in biophotonics are described.

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K13b. **Inherently chiral electrodes, the effective tool for chiral voltammetry**

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An attractive issue in electroanalysis is the development of artificial "intelligent" electrodes, capable to discriminate as well as quantify the enantiomers of chiral analytes, particularly of biological and pharmaceutical interest. For this aim, many approaches have been proposed in the last years. However, even the most successful attempts at chiral discrimination almost invariably resulted in the detection of a difference in current intensity between the signals of the two antipodes of a chiral probe, without differentiation of their redox potentials; the chiral enantioselective layer is in many instances not of general use, but tailored for a given probe; many preparation procedures are very sophisticated and/or the active films fragile.

A winning solution comes from a new class, which we have recently presented and patented[1], of "inherently chiral" molecular semiconductors, in which the coincidence of the element granting both electroactivity and chirality with the entire molecular backbone results in extraordinary chiroptical manifestations, which can be finely and reversibly tuned by the electric potential. Above all, enantiopure electrode surfaces can be easily prepared *e.g.* by electrooligomerization; they mostly consist of *cyclic* oligomers, highly electroactive and chiral, idealizing conducting polymers without ends and of high complexing ability.

Such electrode surfaces are able to discriminate enantiomers of chiral molecules in terms of large peak potential differences (80-200 mV and more), with linear dynamic ranges for peak currents, thus affording enantiomeric ratio evaluation. The same spectacular enantioselectivity is obtained on chemically different surfaces of the same structural concept, which demonstrates the general validity of our proposed strategy. A simple reconditioning protocol affords performing more experiments on a single electrode.The new electrodes have been tested with very good results on chiral probes even very different and of applicative interest[2] (Dopa, methyl-Dopa, ofloxacin, norepinephrine, tyrosine, naproxen, catechines, ascorbic acid...), on different supports, including commercial screen printed ones, and in different media (aqueous and nonaqueous ones, as well as small ionic liquid drops on SPEs).

As an interesting alternative strategy to effective enantiodiscrimination, preliminary results about inherently chiral ionic liquid media applied on achiral electrodes will be also presented.

This work was supported by Fondazione Cariplo (Grants no. 2011-0417 and 2011-1851)

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2015-11-09, Monday

08:00 – 09:00 Breakfast

09:00 – 10:30 **Morning Session 1**
(chairs: Roberto Guzman, Gary Blanchard)

09:00 – 09:40	T12	**Gary Blanchard** Molecular motion as a probe of interface structure. Application from LB films to plasma membranes
09:40 – 10:00	K14	**Roberto Guzman** Controlled drug delivery with polymeric nanoparticles: synthesis, modeling and application in vitro and in vivo pancreatic cancer
10:00 – 10:15	SC09	**Gulnara Safina** Macroporous Indium-Tin Oxide as a Platform for Bio-sensing Applications
10:15 – 10:30	SC10	**Marc Riedel** Chemisorbed DNA-layer for impedimetric DNA detection: Influence of DNA length and Overhang orientation on the hybridization signal

10:30 – 11:00 Coffee Break

11:00 – 12:55 **Morning Session 2**
(chairs: Tan Phat Huynh, Wolfgang Schuhmann)

11:00 – 11:40	T13	**Wolfgang Schuhmann** Harvesting bioenergy - biofuel cells and photobiovoltaics
11:40 – 12:00	K15	**Tan-Phat Huynh** Flexible multi parametric sensors with self-healing properties
12:00 – 12:20	K16	**Caroline Canizzo** Nanostructured and functionalized screen printed electrodes for the detection of metallic pollutants in water
12:20 – 12:35	SC11	**Agata Pomorska** In-situ monitoring of polymer brush film growth on gold as a function of solvent composition by means of Quartz Crystal Microbalance
12:35 – 12:55	K17	**Jingyuan Chen** Current-voltage curves at various diameters of single nanoelectrodes

13:00 – 14:30 Lunch

14:30 – 16:05 **Afternoon Session 1**
(chairs: Elena Ferapontova, Arkady Karyakin)

14:30 - 15:10	T14	**Arkady Karyakin** Advanced biosensors for non-invasive diagnostics
15:10 – 15:30	K18	**Nicolas Plumere** Mechanism for protection of O_2 sensitive catalyst in redox hydrogels
15:30 – 15:50	K19	**Mathieu Etienne** Some strategies for tuning the interaction between bacteria and (nano)materials in electroactive biocomposites
15:50 – 16:05	SC12	**Tomasz Rebis** Redox-active lignosulfonate/conducting polymer composites. Characterization and electroanalytical properties

16:05 – 16:30 Coffee Break

16:30 – 17:40 **Afternoon Session 2**
(chairs: Karsten Haupt, Jahangir Rather)

16:30 – 16:50	K20	**Claire Rossi** EGFR inhibition by curcumin in cancer cells: a dual mode of action - biomimetic and cellular
16:50 – 17:05	SC13	**David Pally** Functionalization of glassy carbon electrode by amines electrochemical oxidation for micro-pollutants detection in water
17:05 – 17:25	K21	**Pawel Krysinski** Effect of Iron Oxide-Based Magnetic Nanocarriers on Model Biomimetic Membranes: Electrochemical and Spectroscopic Studies
17:25 – 17:40	SC14	**Jahangir Rather** Facile Hydrothermal Synthesis of In_2O_3Nanoboxes: Swift Sensing of Parabens

19:00 – 20:00 Dinner

21:00 – ? Disco!

T12. **Molecular Motion as a Probe of Interface Structure. Application from LB Films to Plasma Membranes**

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Interfaces play a key role in essentially all chemical sensing processes, with biosensing requiring structures that are both complex and fragile. Key properties of interfaces include their composition, permeability and fluidity. For plasma membranes, there can be in excess of 1000 distinct species which are thought to be distributed in a non-uniform manner, and it is the ability of these molecular assemblies to control permeability and allow for the diffusive motion of their constituents that determines their utility. Placing such structures on a support facilitates their use for biological and chemical sensing but can lead to a host of other issues, including the strength and nature of interactions with the support, and the ability of the interface to allow for diffusion of imbedded species. In this work we examine the fundamental issues that determine the requisite balance of properties in interfacial structures. We focus on the utility of molecular diffusion as a probe of the robustness and heterogeneity of such interfaces and using model Langmuir-Blodgett-deposited films and a suite of spectroscopic and microscopic imaging measurements, and demonstrate that comparing diffusional motion over widely different length scales affords new insight into these properties.

K14. **Controlled drug delivery with polymeric nanoparticles: synthesis, modeling and application *in vitro* and *in vivo* pancreatic cancer**

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In this research, a variety of drug delivery systems have been synthesized and characterized. For the most part, these consist of a matrix of poly(lactic-co-glycolic acid) (PLGA), polyethylene glycol (PEG), and polyvinyl alcohol (PVA) containing encapsulated anticancer drugs as chemotherapy agents. The drug release from biodegradable nanoparticles has been analyzed mathematically using new approaches that include three major mechanisms of release: initial burst, nanoparticle degradation-relaxation, and diffusion. A mathematical model that simultaneously incorporates these mechanisms was developed to describe the release of the hydrophobic, kinase-inhibitor drug PHT-427. This model considers that the three drug release mechanisms, occur simultaneously, and provide a more accurately description of the release behavior of a real system. The theoretical release studies were corroborated experimentally by evaluating the cytotoxicity effectiveness of PHT-427-loaded nanoparticles over BxPC-3 and MiaPaCa-2 pancreatic cancer cells *in vitro*. These studies showed that the encapsulated PHT-427 drug in the nanoparticles is more accessible and thus more effective when compared with the drug alone, indicating their potential use in treatment applications. In addition, the PHT-427-loaded nanoparticles cytotoxicity was evaluated *in vivo* studies with MiaPaCa-2 pancreatic tumors. The results show that the kinase inhibitor is more effective when is loaded into polymeric nanoparticles compared to drug alone, by reducing MiaPaCa-2 orthotopic pancreatic tumor growth. Also, metastases to the liver are also inhibited by the PHT-427-loaded nanoparticles compared to the polymeric nanoparticle controls (without drug encapsulated) and with the drug alone. The experimental formulation parameters in the synthesis of drug-free PLGA nanoparticles were investigated, in order to find the best conditions of nanoparticle preparation. In addition, a selection of hydrophobic to hydrophilic drugs, such as doxorubicin, PH-427, gemcitabine, and pemetrexed, were encapsulated into polymeric nanoparticles to find optimal drug loadings by using single or double emulsification techniques. The effects of theoretical drug loadings over the nanoparticle characteristics were examined. The release of these drugs from PLGA nanoparticles was evaluated to determine the overall release profile characteristics.

SC09. **Macroporous Indium-Tin Oxide as a Platform for Biosensing Applications**

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Macroporous electrically conductive materials, due to their large active surface area and ability to incorporate higher amounts of biocatalysts, appear to be attractive as platforms for biosensors construction. Furthermore, the possibility to synthesize such materials in controlled fashion by varying pore diameter and film thickness makes them a versatile support for immobilization of biomolecules of wide size range. Different approaches of surface modification and functionalization provide additional possibilities for the development of (bio)sensors with improved working performance.

Here we report the study of immobilization of enzyme cellobiose dehydrogenase from *Corynascus thermophilus* (*Ct*CDH) on the surface of macroporous indium-tin oxide (ITO) glass. It was measured that the macroporous ITO has more than five times higher surface area than the conventional flat ITO glass. Various surface modification approaches have been attempted, such as i) simple physical adsorption of the enzyme onto the macroporous ITO surface, ii) electrostatic attraction of the enzyme to the cationic polymer polyethyleneimine (PEI), and iii) cross-linking of the enzyme with glutaraldehyde (GA). Topography and surface morphology of the enzyme/modifier (PEI or GA) composite was examined using scanning electron microscopy. Efficacy of enzyme incorporation into the macroporous ITO surface was examined using advanced spectroscopy and secondary ion mass spectrometry (SIMS). The presence of the enzyme was confirmed by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). The XPS and SIMS depth profile analysis showed that *Ct*CDH cross-linked with GA penetrates deeper into the pores of the material. In contrast, *Ct*CDH deposited onto the PEI matrix is mainly localized on the surface of the macroporous ITO glass.

The enzyme functionalized microporous ITO electrodes were exploited for the analysis of glucose. Functionalization of the electrode surface with PEI significantly enhanced the enzyme load and led to more than 10-folds increase of the electrochemical response in comparison with the cross-linked enzyme. At the same time, the cross-linking of the biocatalyst exhibited the significantly improved stability in continuous flow-injection measurements. The enzyme macroporous ITO based biosensor demonstrates linear response to glucose within concentration range of 0.125- 20 mM, with limit of detection down to 0.033 mM. The working performance of the constructed biosensor was tested on samples of glucose containing and glucose-free pharmaceuticals.

SC10. **Chemisorbed DNA-layer for impedimetric DNA detection: Influence of DNA length and Overhang orientation on the hybridization signal**

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The development of cost-effective nucleic acid detection systems with a fast applicability and preferably label-free operation have been followed with growing interest during the past decade. A technique which has already shown the potential for label-free determination of DNA hybridization is the electrochemical impedance spectroscopy [1]. While the sensitivity of DNA hybridization and the discrimination of single base pair mismatches was already the subject of various impedimetric studies [2,3], the influence of the target length and the orientation of the target overhang on the impedance signal behaviour haven't paid much attention yet. Therefore we have investigated targets of different length to evaluate the performance and applicability for the detection of PCR products.

For the sensor preparation thiol-modified ssDNA, which serves as the recognition element, was co-immobilized with a short mercaptoalcanol to prevent nonspecific interactions between the DNA and the gold surface. In the presence of the redox system ferri-/ferrocyanide the impedimetric measurements show an increase in charge transfer resistance upon hybridization of ssDNA to the sensor surface. It can be demonstrated that the impedimetric signal stability is influenced by the buffers used during the sensor preparation and the choice of mercapto alcanol compound. Consequently, a stable system is developed enabling specific analysis of hybridization events in a nanomolar concentration range and repeated usage [4]. A further extension of the target length (25mer - 80mer, overhang exposed to the solution) results in a diminished increase of the charge transfer resistance. Investigations by means of surface plasmon resonance spectroscopy indicate that the decrease in impedimetric signal response is not only attributed to a lower hybridization efficiency of longer targets. It suggests, that DNA accumulated near the electrode has a greater impact on the signal than DNA further away. Thus an additional amplification step by a second hybridization at the overhang of the probe-target complex give only minor impedance changes. To accumulate more DNA near the electrode we have changed the recognition sequence position within the target (overhang exposed to the electrode surface). Thereby we find an increased signal response for the same target length. This gives access to label-free detection of long ssDNA as they appear in typical amplification protocols, e.g. PCR, and may also allow the distinction of targets with the same length but different recognition sequence positions.

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T13. **Harvesting bioenergy - biofuel cells and photobiovoltaics**

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The tutorial lecture addresses the fundamentals of energy conversion using biocatalysts. In addition to configurations in which direct electron transfer may occur between the active sites of suitable redox enzymes and electrode surfaces redox polymers are frequently used for wiring biological recognition elements with electrodes. If additionally light-induced charge separation processes are involved such as in systems using the protein complexes of the photosynthetic reaction pathway or if highly oxygen sensitive enzymes such as hydrogenases are used additional constraints have to be taken into account.

The following aspects will be discussed:

1. Electron transfer pathways between redox enzymes and electrodes. Optimization of biofuel cells based on redox-polymer wired bioanodes and biocathodes: How to enable fast kinetics without overpotential losses?
2. Photobioelectrochemistry: How to harvest energy from photosystem 1 or 2?
3. Using hydrogenases in bioanodes: How to prevent damage by oxygen and high applied potentials?

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K15. **Highly-Sensitive Multiparametric Flexible Sensors with Self-Healing Properties**

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The implementation of flexible sensors in real-world applications calls for self-healing properties, in similar way to the human skin. With this in mind, we present here a non-biological and flexible self-healing platform that exhibit sensitivity towards pressure, temperature, and gas analytes. For the sake of demonstration, we report on the fabrication of a complete self-healing device in the form of a bendable and stretchable chemiresistor, where every part of this sensor is self-healing. The device exhibits high sensitivity to pressure (0.11 gF^{-1}) and strain (22.04 mm^{-1}) that are highly comparable to other ordinary technologies. Moreover, the same self-healing platform exhibit sensitivity towards both polar and a-polar volatile organic compounds with a detection limit down to 20 ppb. The self-healing device can be adapted, upon small changes in the architecture, to thermometer that work in the range of 10 to 42 ^{o}C with resolution of 0.1 ^{o}C. Advantageously, analyte, temperature, and pressure sensitivity of this sensor is stable under multi cycles of cutting/healing. The reported self-healing sensor raises expectations that flexible devices might become one day self-administered, thus increasing their reliability in various applications.

K16. **Nanostructured and functionalized Screen Printed Electrodes for the detection of metallic pollutants in water**

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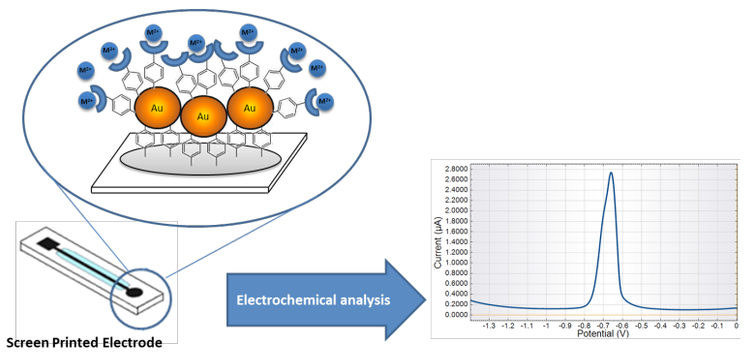
The development of new materials and analysis methods for pollutants in aqueous media is of major concern. In this context, the development of functionalized electrodes can bring many scopes for environmental applications, as they offer cheap, efficient and on-site solutions.

Diazonium salts chemistry[1] has been previously used in our group for the functionalization of Screen Printed Electrodes (SPEs) with carboxylic moieties, leading to sensors able to detect metallic trace elements (MTE such as Cu (II), Pb (II), etc.) at levels near the ppb.[2] The nanofunctionalization of SPEs could be an efficient way to enhance their performances.

In this communication, we will present a covalent grafting method of gold nanoparticles (AuNPs) on SPE surface using diazonium salts chemistry, resulting in a highly nanostructured material. The size and the surface properties of the AuNPs used are key parameters that influence the structuration of the final nanofunctionalized SPEs and accordingly their electrochemical properties.[3]

The synthesis of several diazonium salts, bearing selective complexing groups for several chosen targets, has been realized. These ligands were then covalently grafted on SPEs.

The different results in terms of sensitivity and selectivity obtained with these functionalized nanostructured electrodes will be developed.



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SC11. **In- situ monitoring of polymer brush film growth on gold as a function of solvent composition by means of Quartz Crystal Microbalance**

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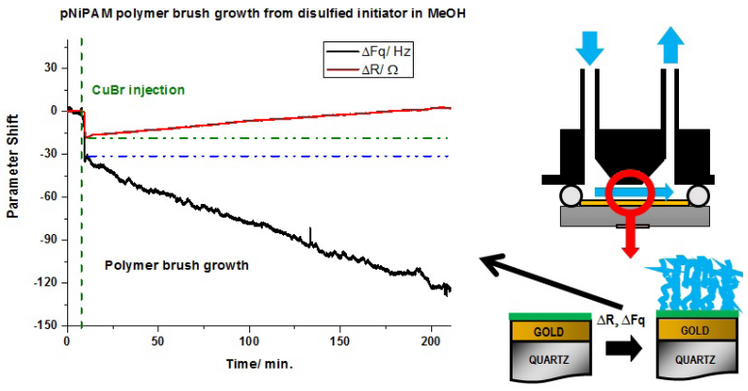
Conductive polymer brushes enable vertical charge transfer[1] on the level of single chains, giving opportunity to enhance efficiency of the future hybrid photovoltaic systems in combination with e.g. ZnO nanocrystalline films.
Such a novel hybrid material can be synthesized through understanding of the polymer brush growth process. Reaction parameters (like monomer concentration and solvent composition) have to be establish to obtain dense high quality organic layer on top of inorganic substrate. One of the most important factors, that influences the process, is solvent composition in which the synthesis proceeds. Poly-N(isopropyloacrylamid) (pNIPAM) was used as a model polymer brush to study its growth via Atom Transfer Radical Polymerization (ATRP) from initiator functionalised gold surfaces. The experiments were conducted via quartz crystal microbalance (QCM)[2]. The device enables simultaneous study of adsorption process and structural changes of the adsorbat. QCM follows frequency and motional resistance shifts of functionalised quartz piezoelectric resonator as a function of time. The substrate were subsequently characterised by means of grazing angle FT-IR Spectroscopy and Atomic Force Microscopy. The experiments were held in water/ methanol mixtures at various ratios as well as monomer concentration. It could be shown that even small changes in solvent composition had a tremendous effect on height and density of the obtained polymer brush films. The overall results pave the way for efficient grafting of conductive brushes from various surfaces.



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K17. **Current-voltage curves at various diameters of single nanoelectrodes**

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This talk reports two characteristics of a single nanoelectrode, (1) extremely high current density and (2) very small current. Both are discussed when current-voltage curves are obtained at various electrode diameters. Both are discussed when current-voltage curves are obtained at various electrode diameters. Our concern is single disk electrodes of which diameters range from 1 nm to 500 nm. (1) The average current density by diffusion control at a microdisk electrode is inversely proportional to the diameter of the electrode. Consequently it increases tremendously with a decrease in the diameter. For example, electrodes 100 nm and 1 nm in diameter generate such high current density that a conventional electrode can produce at scan rates of 20 kV s^{-1} and 200 MV s^{-1} for cyclic voltammetry (CV), respectively. This comparison inspires us to determine fast heterogeneous reaction rate constants under the steady-state conditions. A question is that a common rate constant can be obtained both by steady-state voltammetry at namoelectrodes and by fast cyclic voltammetry at conventional electrodes. We predicted potential shifts of six kinds of redox species with a decrease in the electrode diameter. However, no shift of the current-voltage curves is observed even at 1 nm electrode. Potential shift by CV can be attributed to partially solution resistance and partially dynamic effects of the double layer capacitance. (2) Very small currents at nanoelectrodes allows us to obtain voltammograms of neutral redox species without deliberate addition of salt. When electrodes less than 0.3 mm in diameter are used, sigmoidal current-voltage curves of TCNA in acetonitrile without salt can be obtain. Although voltammograms of TCNQ in the presence of salt show two waves for successive two-electron reduction, non-salt solution shows only the first reduction wave. This behavior is valid also for benzoquinone. Dianions may make complexes with mono-valent cations.

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T14. **Advanced biosensors for non-invasive diagnostics**

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Non-invasive diagnostics is nowadays one of the most important fields of medical diagnostics, because it presumes that during the analysis not only blood vessels, but also skin surface cannot be broken, which completely avoids both infection and trauma of patients. Despite great efforts put in this field, even relative diabetes (detection of glucose concentration in blood) the problems with non-invasive diagnostics cannot be recognized as solved. The lack of success in application of physical (spectroscopy) methods for non-invasive detection of key blood metabolites (glucose, for example) provides the use of chemical analysis.

Fundamental problem is a discovery of the excretory liquids containing key metabolites in concentrations, which are relative to blood concentrations. Here the diagnostic values of sweat and exhaled breath condensate (EBC) are discussed.

Diagnostic value of sweat relative hypoxia is already shown by us (1): relative sweat lactate increase in case of hypoxia correlates with the rise of blood lactate. However, lactate content in sweat is approximately 10 times higher than in blood, which makes impossible the use of conventional lactate biosensors.

Lactate biosensor with the remarkably increased upper detection limit suitable for analysis of undiluted sweat has been elaborated by engineering of the enzyme lactate oxidase upon its immobilization from water−isopropanol mixtures with the high (90%) content of organic solvent (2). To decrease the enzyme binding constant the substrate binding sites in its active center has been shielded with negatively charged polyelectrolyte. The elaborated biosensor is characterized by the calibration graph shifted for 2 orders of magnitude toward high analyte concentrations. The biosensor displays stable response during 4 h of continuous operation. The achieved analytical performance characteristics allow the monitoring of lactate content in undiluted sweat collected directly from the skin surface.

The diagnostic values of EBC concerning hypoxia and hypo-/hyperglycemia will be also discussed.

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K18. **The Mechanism for Protection of O_2 Sensitive Catalyst in Redox Hydrogels**

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Redox hydrogels were developed for the integration of redox enzymes in bioelectrochemical devices toward technological application. High loading in protein is possible via physical entrapment within the hydrogel matrix and finely tuned redox relays allow for fast electron transfer at low overpotential (see for example (1)). The concepts were successfully applied in biosensor construction. The hydrogel were also proposed to serve as matrix to support catalysts for energy conversion or industrial synthesis. Biocatalysts, in particular hydrogenase for H_2 evolution or oxidation, are highly active but suffer from deactivation induced by oxygen. Here we tune the hydrogel properties to provide a protection mechanism for the biocatalysts. The electron relay, beyond its role in electron transfer, induces a redox buffer and serves as catalyst for oxygen reduction (2). Within the hydrogel, electrons are generated from hydrogenase catalyzed H_2 oxidation and are shuttled to the hydrogel - solution interface for O_2 reduction. Hence, the deactivating molecules do not reach the hydrogenase which remains fully active even in presence of an O_2/H_2 mixed feed. The protection mechanism is independent of catalyst reactivation processes as demonstrated by electrochemical modeling (3) and the used of an irreversibly deactivated FeFe-hydrogenase (4). We illustrate the technological relevance with a biofuel cell designed to mimic the harsh conditions encountered in energy conversion applications.

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K19. **Some strategies for tuning the interaction between bacteria and (nano)materials in electroactive biocomposites**

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Bacteria form generally biofilms in environment that can be defined as a community of aggregated bacteria embedded in a polymeric matrix. By this way, they exhibit properties and resistances that they do not express in planktonic state. Interesting property of biofilm is electron transfer via redox reactions, basis of living metabolism. Especially the extracellular electron transfer (EET) happening between bacteria and extracellular acceptor in biofilm allows conduction of electrons from the bacteria to a final solid electron acceptor.

When the support of the biofilm is an electrode, it is possible to take advantage of electron transfer reactions to produce electricity, i.e. in a microbial fuel cell configuration, or to produce an electronic signal, i.e., in the form of a bioelectrochemical sensor. Natural systems are not particularly optimized for these human-sourced applications and there is an interest in developing artificial biocomposite bacterial films, to improve them. Electroactive artificial biofilm could be here defined as a structure mimicking natural biofilm in which a controlled bacteria population is immobilized at the surface of an electrode in order to promote electron transfer reactions.

We have investigated the design of biocomposite comprising *Shewanella oneidensis* or *Pseudomonas fluorescens*. The goal of this work was to promote biocomposite formation, bacterial viability and electron transfer reactions between electroactive bacteria, electron mediator and conductive materials. Different strategies have been evaluated in order to mimic natural biofilms, including loosely-bound cytochrome c or nanowires. We will see that in biocomposites it becomes critical to control the interface between individual bacteria and nanomaterials if one want to promote high viability or current. Tuning the interactions of bacteria with an electrode is also essential when considering imprinting approaches for analytical applications. These different biotechnological aspects will be discussed.

SC12. **Redox-active lignosulfonate/conducting polymer composites. Characterization and electroanalytical properties**

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Redox–active polymers are important class of materials used in the development of chemically modified electrodes for electrocatalytic, electrochemical and bioelectrochemical sensing purposes. Redox polymers contain electrostatically and spatially localized redox sites which undergo reversible oxidation–reduction transitions and the electrons are transferred between adjacent redox sites via electron hoping or by physical motion of the redox centers.

Among large diversity of suitable redox polymers, those containing quinones have received the greatest attention, because of fast two-proton/two-electron transition in broad range of pH, high theoretical capacity, high electron transfer kinetics, excellent redox reversibility, low cost and common occurrence in green plants. Recently a great interest in the application of biopolymers such as lignin and their derivatives (lignosulfonates) in the development of electrochemical devices can be observed.[1,2] Lignosulfonates being a water soluble by-products of pulp and paper industry were used as a electroactive materials and showed strong electrocatalytic behavior toward biomolecules. This activity is attributed to the existence of many phenolic and methoxyphenolic functional groups that can be easily converted into reversible quionone/hydrquinone redox moieties. Thus, lignosulfonates can be classified as a poorly defined quinone based redox polymers. Although lignosulfonate is being increasingly used today, only small percentages have been utilized for the preparation of value-added products. Lignosulfonates as polyanions are easily dissolved in water and its application are mostly carried out in aqueous solutions. These properties enable to use lignosulfonate as an electroactive doping agent of conducting polymers.[3]

The aim of the present work is the electrochemical synthesis of conducting composites comprising lignosulfonates for electrocatalysis, and energy storage applications. For this purpose, relatively simple functionalization of conducting polymers such as: polyaniline, poly-3,4-ethylenedioxythiophene (PEDOT and polypyrrole has been applied, where during galvanostatic polymerisation, lignosulfonate acts as a doping agent. In all cases, significant improvement of surface confined redox signals has been observed, because of development of a reversible couple assignable to quinone/hydroquinone moieties. The combination of conducting polymers and lignosulfonate makes it possible to obtain thin polymeric films showing electrocatalytic properties towards the oxidation of dihydronicotinamide adenine dinucleotide (NADH), hydrazine and ascorbic acid.

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K20. **EGFR Inhibition by Curcumin in Cancer Cells: a dual mode of action - biomimetic and cellular approaches**

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The Epidermal Growth Factor Receptor (EGFR) is a 170-kDa transmembrane protein with an intracellular tyrosine kinase activity, which is stimulated by the receptor dimerization. Binding of specific ligands leads to receptor dimerization and tyrosine kinase autophosphorylation, which is the first and crucial step for signaling. EGF receptor is an important target of anticancer therapy, as its abnormally high tyrosine kinase activity play key roles in the development of many tumors. Nowadays the search for new molecules inhibiting this receptor is turning towards natural substances. One of the most promising natural compounds that have shown an anti-EGFR activity is curcumin, a polyphenol found in turmeric. Its effect on the receptor kinase activity and on the receptor autophosphorylation has been already described, but the mechanism of how curcumin interacts with EGFR is not fully elucidated.

We studied the mechanism of early curcumin action on EGFR autophosphorylation by different approaches. EGFR were reconstituted in biomimetic lipid membrane platforms that allow measuring the EGFR dimerization and its autophosphorylation resulting from its inherent tyrosine kinase activity in simplified, non denaturing, fluid and oriented conditions.[1] This artificial membrane models provide a convenient tool to both qualitatively and quantitatively elucidate the mechanism of activation and inhibition of EGFR. In parallel, the effect of curcumin on EGFR activation was studied *in vitro* on separate EGFR domains and on human epidermoid carcinoma cells. The impact of curcumin on the fluidity of the lipid bilayer and the diffusion coefficient of EGFR into the cell membrane, which constitutes the direct environment of EGFR, were investigated as well.[2]

Thanks the combination of these different approaches, we highlighted that the curcumin acts as an inhibitor with a dual action mode: by direct inhibition of the tyrosine kinase activity but also by modulation of the lipid bilayer-mediated EGFR monomer association.

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SC13. **Functionalization of glassy carbon electrode by amines electrochemical oxidation for micro-pollutants detection in water**

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Good chemical status of European water is defined in terms of compliance with all the quality standards established for chemical substances at European level in the European Water Framework Directives (WFD) [1]. Implementation of the WFD needs the monitoring of 45 micro-pollutants belonging to several chemical groups such as metal, HAP, pesticide, hormone...For now, all the controls need on site sampling then analysis in laboratory that require costly apparatus. Consequently, the spatial and temporal cover of the monitoring plan remains inadequate. The improvement of water quality involves the implementation of self-powered on-site devices of analysis with remote data collection. Electrochemical sensors are good candidate to meet these specifications. However the improvement of the sensibility, the robustness and the selectivity of the electrode is essential to allow the development and the validation of the electrochemical sensors as standard tools for water monitoring.

Within this context, our works deal with the development of functionalized carbon electrodes for micro-pollutants detection in aqueous media. Especially we have shown that electro-grafted carboxy-carbon electrode via reduction of diazonium are able to detect metallic micro-pollutants such as Cu(II), Pb(II), U(VI) or Cd(II) at ppb levels[2].

In this presentation, the electro-oxidation of several amines is explored as functionalization way to improved selectivity and sensibility of glassy carbon electrode used for lead detection. Since 1990, electro-oxidation of primary and aromatic amines is known to be able to grafted organic layer on carbon, noble metal and semiconductor. Less used as surface modification method than the electro-reduction of diazonium salt, this way allows grafting of covalent layer and is an powerful alternative to functionalize carbon surface by aliphatic or aromatic groups.

In the present work, we functionalized glassy carbon electrode by carboxyl groups via oxidation of the corresponding amines and we will show their potential application to trace lead detection. Evidence of the grafted layer at the electrode surface was investigated via electrochemical signal study of the ferri cyanide probe. XPS and FTIR characterization are used to show the presence of the carboxyl function on the glassy carbon grafted surface. The roughness and the homogeneity of the grafted layer are explored by AFM. Analytical performances of the carboxy grafted glassy carbon electrode will be established for the analysis of lead aqueous solution. Finally a comparison will be proposed between the performances of the grafted electrode obtained via electro-oxidation of amines and electro-reduction of the corresponding diazonium salts.

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K21. **Effect of Iron Oxide-Based Magnetic Nanocarriers on Model Biomimetic Membranes: Electrochemical and Spectroscopic Studies**

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The objective of this work is to gain fundamental insight into the interactions of superparamagnetic nanoparticles with biomimetic interfacial structures of molecular thickness. Such nanoparticles are used as nanocarriers in the targeted drug delivery or magnetothermal therapy, both aided by the external magnetic field. We have systematically studied the passive permeation of these nanocarriers across the lipid mono- and bilayers of different organization, monitoring the nanoparticle (SPION – superparamagnetic iron oxide nanoparticle) interactions with the hydrophilic part of the monolayer and then, separately, with its hydrophobic moiety. Using electrochemical techniques, and the impedance spectroscopy in particular, we investigated these interactions, likely competing in a native membrane, for the case of Langmuir monolayers, Langmuir-Blodgett monolayers, and supported bilayer lipid membranes, exposed to SPIONs in an aqueous solution. This gave us a unique possibility to monitor the SPION interactions with different regions of biomimicking film. Further information was gained from spectroscopic data that provide a complementary picture to the electrochemical ones. Both types of measurements required the spectroscopically active reporter molecules integrated within the biomimetic layers. For these purposes we used biomimetic mono- and bilayers formed from lipids tagged with Rhodamine B in their hydrophilic headgroups. While the electrochemical data provide significant insight into the ability of SPIONs to interact with biomimetic interfacial structures, the time- and frequency-resolved spectroscopic measurements and fluorescence lifetime and anisotropy imaging (FLIM/FAIM) data point collectively to the extent of organization of the interfaces we have formed, under the influence of magnetic nanocarriers. These data are supplemented by surface-enhanced resonance Raman scattering (SERRS) results.

Our initial findings, demonstrate that such experiments can distinguish between the molecular-scale interactions of the nanoparticles with tagged lipid films with the polar head groups and the aliphatic nonpolar moiety of biomimetic films. Thus, every step of interactions: adsorption, penetration and partitioning can be spatially resolved and monitored also in the time domain. This complex, complementary approach, in which both regions of the biomimetic membrane can be detailed separately, and the interactions between SPIONs and biomimetic surfaces can be followed at all relevant length and time scales, highlights the pioneering aspect of this presentation.

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SC14. **Facile Hydrothermal Synthesis of In_2O_3 Nanoboxes: Swift Sensing of Parabens**

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Novel indium oxide (In_2O_3) nanoboxes have been prepared by template-less and surfactant-free hydrothermal synthesis. Synthesized In_2O_3 nanoboxes were characterized by X-ray diffraction (XRD) and field emission scanning electronic microscopy (FESEM). FESEM micrographs revealed highly uniform nanoboxes with smooth surfaces and XRD analysis confirmed that these In_2O_3 nanoboxes grown with a cubic crystal structure. The synthesized In_2O_3 nanoboxes were successfully immobilized on the surface of glassy carbon electrode for the detection of Parabens (butylparaben). Owing to the unique structure and intriguing properties of these In2O3 nanoboxes, the film electrode has shown an obvious electrocatalytic activity for the detection of butylparaben and the detection limit (LOD) was estimated to be 0.08 µM. This sensor showed high sensitivity compared with other electrochemical sensors reported so far for the detection of butylparaben.

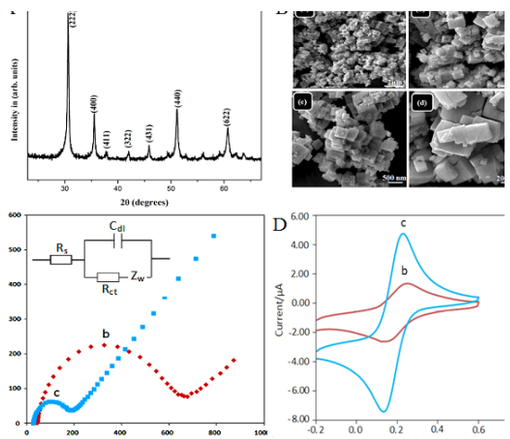

Figure 1: Characterization of Indium Oxide Nanoboxes and Fabricated sensor In_2O_3/GCE

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2015-11-09, Tuesday

08:00 – 09:00	**Breakfast**

09:00 – 10:10 **Morning Session 1**
(chairs: Frank Marken, Piyush Sindhu Sharma)

09:00 – 09:40	T15	**Frank Marken** Intrinsically microporous films and membranes in electrochemistry
09:40 – 9:55	SC15	**Alexandra Lipka** Investigation of the Protease-activated Receptor (PAR)1 on Thrombocytes using Single Molecule Force Spectroscopy
09:55 – 10:10	SC16	**Piyush Sindhu Sharma** Electrochemically Synthesized Molecularly Imprinted Polymers for Selective Determination of Biomarker Compound

10:10 – 10:30	**Coffee Break**

10:30 – 11:40 **Morning Session 2**
(chairs: Andreas Ebner, Lo Gorton)

10:30 – 10:50	K22	**Andreas Ebner** Sensing Molecular Interactions in Nanomedicine on the Single Molecule Level
10:50 – 11:30	T16	**Lo Gorton** Bioelectrochemical studies of photosynthetic cells and membranes on electrodes
11:30 – 11:40		**Closing**

12:00 – 13:00	**Lunch**
13:00 –	**Departures**

T15. **Intrinsically Microporous Films and Membranes in Electrochemistry**

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Polymers with Intrinsic Microporosity (PIMs) provide a novel class of structurally rigid ion-selective membrane materials with 3D nanofluidic pores of typically 15 nm size. The PIM-EA-TB material employed here is based on a poly-amine with estimated $pK_{A1} = 4.0$ and $pK_{A2} = 0.4$ and therefore in the protonated state an anion-conductor. The microporous material can be employed to "heterogenise" water-insoluble molecular redox systems in films at the electrode surface [1,2]. When deposited asymmetrically over a 20 mm diameter hole in poly-ethylene-terephthalate (PET) and investigated in a two-compartment electrochemical cell with aqueous electrolyte on both sides, ionic diode effects [3] (associated with pK_{A1}) are observed with potential applications in iontronics and water desalination [4].

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SC15. **Investigation of the Protease-activated Receptor (PAR)1 on Thrombocytes using Single Molecule Force Spectroscopy**

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Cardiovascular disease is the leading cause for morbidity and mortality in all developed and industrialized countries. Platelets have been considered central in the development and course of this disease. These anucleate blood-borne particles are responsible for blood clot formation once the coagulation cascade is started. Enhanced platelet reactivity is associated with an increased progression of atherosclerotic disease, and it is also responsible for the occurrence of acute vessel occlusion leading to myocardial infarction, stroke and death. A key player in the activation cascade is the serine protease thrombin, acting as the most potent platelet agonist. Together with GPIbα, a complementary trimeric receptor, a complex is formed regulating platelet activation by thrombin that enables thrombin to act as a bivalent or even trivalent functional agonist.

Within this study we investigated the PAR1 receptor embedded into the cellular membrane by performing single molecule force spectroscopy experiments. For this, single molecule sensors using a heterobifunctional poly(ethylene) crosslinker were generated by tethering an single anti PAR1 antibody to the outer tip apex. Two different IgGs were used, one binding the cleaved, and the other one binding only the non-cleaved PAR1 receptor. This provides direct information on the activation state of PAR1 and is highly relevant in the clotting cascade. Further experiments, especially using recognition imaging are ongoing and will help to reveal the relevance for the PAR mediated pathway in thrombosis and anti-thrombotic therapy.

SC16. **Electrochemically Synthesized Molecularly Imprinted Polymers for Selective Determination of Biomarker Compound**

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Conducting polymers in their oxidized state are doped with anions.[1] This doping exploits selective recognition sites for small anions in a polymer.[2] This doping idea is now more and more frequently used in the field of molecular imprinting of ions and, moreover, neutral compounds.[2-3] However, the selectivity of the resulting films serving as recognition units is unsatisfactory.

With an established procedure of molecular imprinting, a synthetic receptor for the neopterin cancer biomarker was prepared and used as a recognition unit of a potentiometric chemosensor. Biomarkers are indicators of some cellular biochemical or molecular alterations that are measurable in biological media, such as tissues, cells, or fluids. In clinical practice, biomarkers aid in prediction, identification of cause, regression, or outcome of a treatment of disease.[4] For instance, neopterin is considered as a biomarker of a pro-inflammatory immune response serving activation of a cellualr immune system in malignant diseases.[5]

To prepare synthetic receptor for neopterin biomarker, *bis*-bithiophene derivatized with cytosine and bithiophene derivatized with boronic acid were used as functional monomers. Open circuit potential (OCP) based transduction under flow-injection analysis conditions (FIA) determined neopterin in the concentration range of 0.15 to 2.5 mM with the 22 μM detectability and 7.01(±0.15) mV mM^{-1} sensitivity. The recognition MIP film showed appreciable imprinting effect and the chemosensor sucessfully descriminated several interferences including the 6-biopterin and pterin structural analogues of neopterin.

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K22. **Sensing Molecular Interactions in Nanomedicine on the Single Molecule Level**

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Single biomolecules (e.g. antibodies) are able to specifically recognize and bind their corresponding partner with high efficiency. This process is known to play a pivotal role in biology, physiology and medicine. From the chemical point of view bio-recognition can be described as a combination of non-covalent weak interactions including electrostatic (ionic), hydrophobic, and van der Waals interactions as well as hydrogen bonding. Furthermore, steric aspects, especially the complementary structure of the two binding partners, are highly relevant for complex formation and stability. Taken together all these aspects determine both, the strength and the characteristic lifetime of the bond. To determine receptor ligand interactions on the molecular level, the atomic force microscopy (AFM) based molecular recognition forces spectroscopy (MRFS)(1) offers the most versatile approach to explore forces during the bio-recognition processes at the molecular level. In MRFS the tip of an AFM cantilever is upgraded to a molecular biosensor(2) resulting in a single ligand molecule tethered at the outer tip apex, which is allowed to interact with its corresponding binding partner (e.g. isolated proteins)(3), artificial(4) or native biomembranes(5) or living or fixed cells(6)). As a result, molecular interaction forces and complete energy landscapes can be explored, gaining insights into structure and function of nanomedical relevant receptor-ligand pairs.

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T16. **Electrochemical Communication between Photosynthetic Membranes/Cells and Electrodes**

Lo Gorton*[a], KamrulHasan[a], Galina Pankratova[a], DónalLeech[b], Cecilia Hägerhäll[a], SinanCemEmek[a], Per-ÅkeAlbertsson[a], Hans-Erik Åkerlund[a], Yusuf Dilgin[c], Michael A. Packer[d], Eva Sperling[a], Peter ÓConghaile[b], HuseyinBekirYildiz[e], DmitriiPankratov[f], Sergey Shleev[f]

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Electrochemical transfer communication between bacterial cells/biological membranes and electrodes can usually be obtained through the use of freely diffusing monomeric redox mediators. Previously we have, however, also shown that flexible osmium redox polymers can work as efficient mediators for a number of both gram– as well as gram+ bacteria [1,2]. As a continuation of our work on bacterial cells [3-8] we have now turned to various photosynthetic organisms/membrane systems. Here we report on electrochemical communication between whole viable photosynthetic bacterial cells (*Rhodobactercapsulatus* [9,10]and*Leptolyngbia*sp. [11].)as well as with eukaryote systems (thylakoid membranes from spinach [12,13], the eukaryote algae *Paulschulziapseudovolvox* [14]) and electrodes through the use of osmium redox polymers. Here we also report on how to increase the efficiency of the charge transfer from the photosynthetic reaction centres to the electrode as well as to increase the stability of the system.

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Posters

P01. **Discrimination of five engineered Cellobiose Dehydrogenase mutants from *Myriococcum thermophilum* covalently attached at carbon nanotubes electrodes**

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Direct electron transfer of redox enzymes that are close to the electrode surface is usually very slow. It may even prove impossible because of the shielding of the active side and/or redox-active cofactors of the enzyme by the surrounding insulating protein shell. This problem can be resolved by introducing multi-cofactor enzymes in which the overall distance between two redox sites is divided into a number of shorter distances (1). As a flavocytochrome, Cellobiose Dehydrogenase (CDH) (EC 1. 1. 99. 18) has been used as a model for glucose biosensor because of its exceptional properties (2).
This study suggests a new approach for the construction of a stable glucose biosensor based on the covalent immobilisation of cysteine genetically engineered Cellobiose Dehydrogenase (CDH) from *Myriococcum thermophilum* onto modified multi-walled carbon nanotubes (MWCNTs). The carbon nanotubes were modified with maleimide groups by using a method introduced in 2014 by Wright *et a l*(3). Five *Mt*CDH mutants have been used in this work, which were engineering modified to bear a free cysteine residue in different positions at the surface of the enzyme, allowing fast and selective attachment to maleimide-modified GC/CNT electrodes.
Cyclic voltammetry experiments with the *Mt*CDH-modified electrodes were carried out in buffered solutions at pH 5.5, which has been shown to be the optimal pH for MtCDH (4), and pH 7.4, the physiological pH, at increasing concentrations of glucose, showing direct electron transfer (DET) between the enzyme and the electrode surface and allowing discrimination between the different *Mt*CDH mutants. Calibration curves for glucose were recorded and the data were fitted to the Michaelis-Menten equation, allowing the determination of kinetics parameters for the five different *Mt*CDH mutants at the two different pHs. Moreover, tests in the presence and absence of calcium chloride and a heme-inhibitor were carried out to reach a better understanding of the DET and MET mechanism of this enzyme.

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P02. **Design of Benzoxazine monomers bearing N6-coortdinated Osmium-complexes for the electrochemical induced deposition of bioactive layers**

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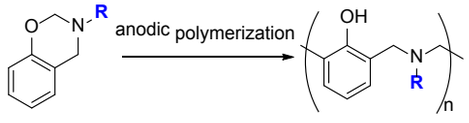
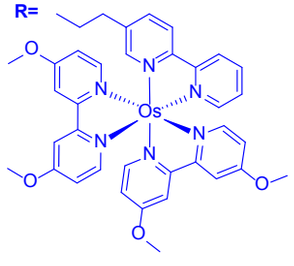
Recently we presented a new family of Os-complex modified poly(benzoxazines) for the wiring of enzymes to electrode surfaces. Os-complex modified benzoxazine monomers could be electropolymerized via a ring opening mechanism of the benzoxazine moiety by applying positive potentials (Figure, left). Co-deposition with glucose oxidase lead to enzyme electrodes that could be successfully used in the amperometric detection of glucose. A change in the formal potentials of the Os-moieties during polymerization was observed which was attributed to labile N-C bonds that are located in the linker chain that connects the complex and the polymer backbone. To improve the stability of the Os-complexes during electrodeposition we synthesized N6 coordinated Os-complexes where the linker for the attachment to the polymer is connected via a stable and inert C-C bond (Figure, right). The electrochemical properties of these new Os-complex modified benzoxazines as well as their deposition onto electrode surface for the immobilization of enzymes will be discussed and compared to our recently obtained results.





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P03. **A synthetic molecularly imprinted polymer (MIP) genetics idea: an artificial TATA box with the TATAAA promoter sequence**

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A new synthetic genetics idea involving a recognition strategy of molecular imprinting was applied to prepare an artificial TATA (T-thymine, A-adenine) box with the artificial TATAAA-promoter sequence. That is, the TATAAA oligodeoxyribonucleotide moiety of the DNA core promoter was selectively recognized by molecular imprinting. For that, two stable electroactive bis(2,2'-bithien-5-yl)methane functional monomers, each bearing either T or A nucleobase, were synthesized and allowed forming a pre-polymerization complex with the TATAAA template via Watson-Crick interactions. Then, this complex was potentiodynamically electropolymerized to deposit a film of the polymer molecularly imprinted with TATAAA (MIP-TATAAA). In our study of amino acid interaction with the MIP film, the film was considered as a matrix of an artificial TATA box with an artificial TATAAA-promoter sequence. This box ability of binding TATA-binding protein (TBP) was verified with the piezoelectric microgravimetry (PM) experiments at the quartz cystal microbalance (QCM). For that, the resonant frequency change of the Au-QCR coated with the MIP film was measured under the FIA conditions, after injecting aqueous solution of just one amino acid, namely, either L-serine, L-lysine, L-glutamic acid, L-asparagine, L-threonine, L-valine, L-phenylalanine, or L-leucine. The mass of a given amino acid interacting with the MIP film, determined with the QCM, indicated the number of moles of the amino acid interacting with an artificial TATAAA-promotor sequence of the artificial TATA box. The number of amino acid molecules per one nucleobase moiety in the TATAAA of the natural TATA box varied in the range of 2 to 7. The number of MIP-TATAAA monolayers available for amino acid permeation were determined from the resonance frequency change of the (amino acid)-(artificial TATAAA-promoter) interactions. Our present preliminary results, in which amino acids interact with the artificial TATAAA promoter, are encouraging to spur a variety of biochemical studies of the MIP interactions with basal transcription machinery and the (transcription factor)-DNA complexes. Our results usher us in a new era in synthetic genetics to find a widespread use in biotechnology and molecular medicine including answers to basic issues of the transcription origin.

P04. **Third Generation Lactose Biosensor Based on *Corynascus thermophilus* Cellobiose Dehydrogenase Immobilized on New NPs Based Electrodes**

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The field of nanotechnology is one of the most active areas of research in modern materials science. New applications of nanoparticles (NPs) and nanomaterials are emerging rapidly. Green synthesis provides advancement over chemical and physical methods as it is cost effective, environment friendly, easily scaled up for large-scale synthesis and further there is no need to use high pressure, high temperature, energy, or toxic chemicals. Synthesis of NPs using biological entities has great interest due to their unusual optical, chemical, photoelectrochemical and electronic properties. One of the most considered methods is the production of metal NPs using biological systems such as microbes, fungi and several plant extracts (1).
In this work, we have synthesized metallic NPs using quercetin, a flavonol contained in some foods and drinks like red onion, black tea and red wine. After a preliminary characterization using UV-Vis spectrometry, transmission electron microscopy (TEM), dynamic light scattering (DLS), and energy dispersive X-ray diffraction (EDX) (2), we used the metal NPs, i.e., gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), to study if it is possible to increase the direct electron transfer (DET) properties of *Corynascus thermophilus* cellobiose dehydrogenase (*Ct*CDH) when such NPs are used to modify spectrographic graphite electrodes (SPGE) (3).
First of all, the electrocatalytic current has been measured for SPGE/*Ct*CDH, SPGE/AuNPs/*Ct*CDH and SPGE/AgNPs/*Ct*CDH with β-lactose as substrate, and then we used the NPs based electrodes as sensors in a flow injection analysis system to calculate Michaelis-Menten constant (K_M), turnover number (k_{cat}) and maximum current (I_{max}).
These new NPs based *Ct*CDH electrodes, have also been characterized as bioanodes in a biofuel cell set-up.

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P05. **Composite BDD-RTIL electrode for the quantification of nafcilin in real samples**

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β-lactam antibiotics are a large group of drugs used in modern medicine, for the treatment of diseases in food-producing animals. However, accumulation of antibiotics in food and enviroment has been implicated in the occurrence of resistant bacterial strains, causing a threat to public health. Subsequently, their use in the farming of food producing animals has been strongly regulated. So it is important to have reliable and fast analytical methods to assess the presence of these compounds in real matrices. Even if many different analytical techniques have been employed for β-lactam determination, the currently available tests encounter problems with a selective detection of nafcillin, an antibiotic that belongs to the family of penicillins [1-2]. To overcome this limitation a chemical sensor for determination of nafcillin in real samples is presented here, employing Boron Doped Diamond (BDD) electrodes, modified with a film of $BMIM^+BF_4^-$, a Room-Temperature Ionic Liquid (RTIL). The direct electrochemical detection of penicillin antibiotics on bare BDD has been recently reported (3). However the use of RTIL films allows to pre-concentrate the target analyte from the solution (4), avoiding extensive sample pretreament. Also the fast electron transfer kinetics of RTIL-modified electrode could be useful to enhance the signal, lowering the LOD (5). The RTIL film is formed on BDD electrodes by simple deposition of the solution on the surface and subsequent evaporation of the solvent. The surface of the modified electrode is then characterized by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) with $Fe(CN)_6^{4-}$/ $Fe(CN)_6^{3-}$ redox couple. After the characterization, the modified electrode was used for the analysis of nafcillin antibiotic in solution. After an accumulation step (150s at open circuit potential under stirring), the LSV/DPV spectra were acquired between 0.2 and 1.4 V in acetate buffer 0.1M pH4. The proposed sensor was tested in samples of tap water and milk spiked with different concentration of nafcillin.

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P06. **Resistance and Asymmetrical Current Effects in the Q^{224} Meosphase of Phyantriol**

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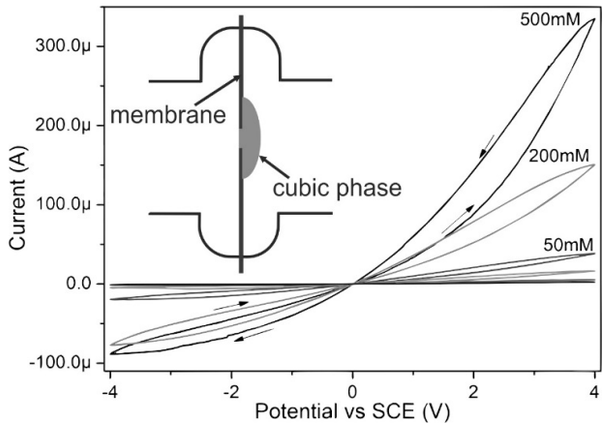
Recent studies into ion transport within cubic mesophases focus on processes involving large proteins, drugs and redox active ions (1,2). These studies reveal information about particular compounds but largely use a substrate that can introduce undesirable surface interactions. Here we present the results of resistance and ion transport measurements on the Q^{224} cubic mesophase of phytantriol using a 4-electrode membrane cell with KCl solutions. The resistance of a pore, bare and covered in cubic phase, is determined by low bias cyclic voltammetry and impedance spectroscopy. Compared to the open pore the resistance increases by an obstruction factor of 0.8 in the cubic phase, close to the expected value from the self-diffusion theory of Anderson et al. (3).



At higher bias voltages asymmetric current responses are observed consistent with ionic diode effects (4). For phytantriol Q^{224}, voltammograms exhibit distinct asymmetry. With large positive bias higher currents were achieved in contrast to negative bias, where smaller currents further decreased after applying the maximum negative bias. Effects are attributed to possible alignment and surface tension effects of the lipid mesophase in a high electric fields.

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P07. **Characterization of Redox Enzymes Immobilized on Electrodes in a Monolayer and Within a Solvated Redox Matrix.**

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The immobilization and electrical contacting of redox enzymes on electrode surfaces or in films is driven both by fundamental studies and by technological applications. For this purpose, electroanalytical methods are powerful tools which are oftentimes used to identify the mechanism and to quantify the diffusion and reaction processes which contribute to the bioelectrocatalytic current (1).
Fundamental studies are often based on a monolayer of the protein either under direct electron transfer or by mediated electron transfer with the electrode. In these studies, the relevant kinetic and thermodynamic information is extracted under various experimental conditions. Here we show how the bioelectrocatalytic properties of ferredoxin NADP+ oxidoreductase monolayers on an Au electrode can be fully characterized my means of cyclic voltammetry. To this end, we quantify the kinetic and equilibrium related constants which define the catalytic properties of the enzyme. These important parameters are determined both under homogeneous conditions and when the enzyme is confined to the electrode surface. The comparative study reveals that neither the activity of the enzyme nor the mediated electron transfer are hindered when the protein is immobilized on the surface. However, hindered substrate diffusion, due to the orientation of the enzyme in which the active site faces the electrode surface, limits the overall catalytic performance.
In technological applications, the redox enzyme is often integrated into a solvated matrix such as redox hydrogel, which allows for the achievement of high loading and of protein stabilization. Electrochemical methods are again used to identify the mechanism defining the catalytic current and to quantify the reaction and diffusion processes. Calculation of the time-dependent concentration profiles can also give important insights into the system, as was done for the case of hydrogenase immobilized in a redox hydrogel (2). Both the current limiting processes as well as a protection mechanism could be elucidated with the help of electrochemical modeling and simulation.

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P08. **Extended-gate field-effect transistor (EG-FET) as the transducer in a chemosensor for stereoselective D- and L-phenylalanie determination**

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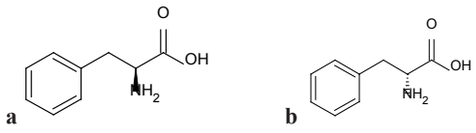
Herein, molecular imprinting combined with the extended-gate field-effect transistor (EG-FET) transduction was used for stereoselective recognition of phenylalanine. Phenylalanine is an a-amino acid present in human body as an L-enantiomer (Scheme 1). The deficiency or excess of phenylalanine in the organism is dangerous. The excess is especially threatening for people with the phenylketonuria (PKU) genetic disorder. Individuals with this disorder must control their intake of phenylalanine (1).

The EG-FET is another FET structure, which allows isolating the transistor from chemical environment. In this structure, a chemically-sensitive film is deposited on the electrode extended from the FET gate for sensing applications (2,3).

Molecular imprinting is widely used for preparing synthetic polymers that contain predetermined molecular cavities with selective sites recognizing and capturing desired template molecule. Molecularly imprinted polymers (MIPs) are synthetic polymers with highly selective recognition ability for target analytes. In the most common preparation procedure, functional monomers form a pre-polymerization complex with a template through either covalent or non-colvent interactions and are joined by a cross-linking monomer to form a polymer(4).



Scheme 1. Structural formula of (a) L- and (b) D-phenylalanine.

We devised a sensing system stereoselective with respect to D-phenylalanine by using an MIP thin film as the recognition unit. This film was deposited by potentiodynamic electrochemical polymerization of the tailor-designed bis(bithiophene)-based functional monomers, in the presence of the D-phenylalanine template, on the surface of an extended gate of a commercial MOSFET. The template removal was confirmed with the differential pulse voltammetry measurements. The binding of the phenylalanine chiral analytes by compatible molecular cavities was transduced by the EG-FET, at a constant gate voltage, as a source-drain current. The devised chemosensor successfully discriminated D- and L-phenylalanine.

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P09. **Selective electrochemical sensing of human serum albumin by semi-covalent imprinting**

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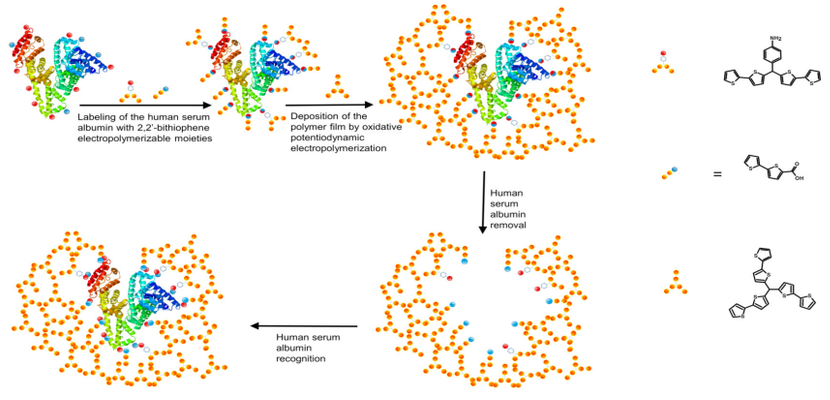
We devised and fabricated a conducting molecularly imprinted polymer (MIP) for human albumin (HA) determination using semi-covalent imprinting (Scheme 1). The bis(2,2¢-bithien-5-yl)methane units constituted the MIP backbone. This MIP was deposited as a thin film on an Au disk electrode by oxidative potentiodynamic electropolymerization. The HA template imprinting, and then its releasing from the MIP was confirmed by the XPS and PM-IRRAS measurements as well as by AFM imaging. The DPV and EIS response to the HA presence in a test solution of the MIP film coated electrode was linear in the range of 0.8 to 20 and 4 to 80 µg/mL HA, respectively, with the limit of detection of 16.6 ng/mL and 0.8 µg/mL HA, respectively. The semi-covalent imprinting provided a very well defined location of recognition functionalities in the MIP molecular cavities. Those were placed only on surface of the imprinted molecular cavities and the polymer surface. The MIP selectivity against low-molecular interferences, common for body fluids, such as blood and urea, was very high. The MIP was not responsive to their presence at concentrations encountered in natural samples. Moreover, selectivity of the MIP film coated electrode with respect to macromolecular interferences, such as myoglobin and cytochrome *c*, was excellent while to lysozyme was slightly lower but still high.



Scheme 1. Molecular imprinting of human serum albumin in a bithiophene conducting polymer.

P10. **MoS_2 nanopetals as effective scaffold for gold nanoparticles. Synergistic electrocatalytic effect.**

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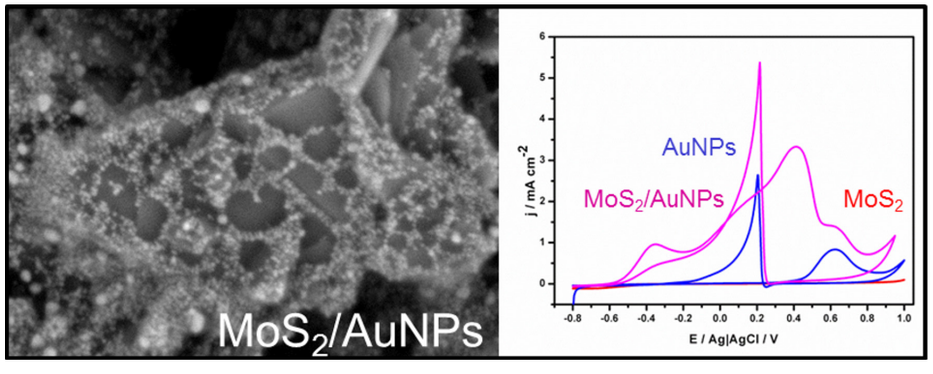
Synthesis of new nanohybrid materials and exploration of their synergistic behaviours are of high importance in the field of electrocatalysis, mainly for their potential applications insensing and energy conversion. Here, MoS_2 nanopetals stacks bearing partial negative charge were decorated with positively charged gold nanoparticles (with mercaptoalkylammonium functionalities of two different lengths) *via* droplet deposition of individual components on indium tin oxide plates. The higher coverage density of gold nanoparticles with shorter alkyl chain functionalities on MoS_2 nanopetals stacks was evidenced by scanning electron microscopy and X-ray photoelectron spectroscopy. IR spectra of these hybrid materials is typical for gold nanoparticles. Synergistic electrocatalytic properties of these hybrid materials towards the oxidation of biologically relevant compounds such as cysteine, glutathione and glucose were demonstrated by significant shifts of the onset oxidation potentials and higher current densities.



P11. **Combination of laccase and catalase in construction of hydrogen peroxide biosensor**

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Our aim was to prepare a stable biosensor for the detection of hydrogen peroxide. The biosensors were obtained by modifying glassy carbon electrode (GCE), screen printed electrode BVT and carbon paper functionalized with naphtylated carbon nanotubes and adsorbed enzymes. Catalase from bovine liver is a heme-containing redox enzyme known for its ability to degrade hydrogen peroxide to form H_2O and O_2. Laccase *Trametes versicolor* is a multicopper enzyme catalyzing the reduction of oxygen directly to water. Carbon nanotubes increase the working surface of the electrode and provide direct contact with the active sites of laccase. We used catalase as a generator of oxygen in H_2O_2 solution. Oxygen formation was monitored by the CNTs/ laccase film electrode. The results of cyclic voltammetry and chronoamperometry experiments show the synergy of enzymes - laccase and catalase immobilized on the carbon nanotubes. Both enzymes are active and more importantly do not inhibit each other. The presented biosensor will be tested in a system powered by a biobattery and a biofuel cell (1, 2).

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P12. **Chemisorption of simple dithiocarbamate derivatives as a strategy of gold transducers functionalization**

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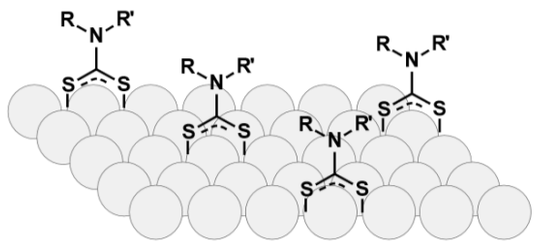
The development of biosensors, whose design is based on a transducer modified with biologically active layer, which is capable of specific molecular recognition of an analyte, is the most intensively growing area of bioanalytics. Currently, the most popular method of biosensors design is based on immobilization of receptors bearing a thiol moiety. However thiol-based monolayers have several drawbacks, such as sensitivity to oxidation or the presence of thiols in a sample, and a poor ability to transfer electrons. Minimization or elimination of these shortcomings could reflect in biosensors, which could be used for the analysis of complex samples and reduce the demands on the storage and analysis conditions.

Dithiocarbamates (DTCs) are salts of dithiocarbamic acids. DTCs are formed in the nucleophilic substitution reaction, in which a primary or secondary amino group (that serves as a nucleophile) is reacted with carbon disulfide. The above mentioned reaction proceeds spontaneously at slightly alkaline pH, which is necessary to deprotonate the amino group (1).

Dithiocarbamate monolayer could be an interesting alternative to the thiol monolayers also due to the greater stability of the formed monolayer. DTC-gold bond characterizes itself with a small and well-defined distance of the two bonding sulfur atoms and therefore it is less labile and more resistant to desorption in comparison with the thiol equivalent. DTC are not capable of forming monolayers of high density. This fact hampers a non-covalent interaction between the chains, which results in lower density and smaller degree of order (2,3).

In the framework of presented study, ability of DTC derivatives to chemisorption on gold, depending on parameters such as pH or modifier concentration, was examined. Properties of chemisorbed monolayers (DTC and thiol-based) and possibly similar in construction, physically adsorbed ones on gold electrodes were compared. Then, properties of the resultant layers were characterized by cyclic voltammetry and differential pulse voltammetry. Another goal was to optimize conditions for the synthesis of dithiocarbamates with simple amine derivatives. Additionally, long-term stability of DTCs in solutions was also studied.



Chemisorption of DTCs on gold.

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P13. **Lactate Biosensing of Adsorbed Lactate Dehydrogenase on Polyelectrolyte Modified Carbon Nanotubes**

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Monitoring the concentration of lactate may be successfully utilized in preparing appropriate training programs for athletes. Moreover, blood lactate is proven to be clinically valuable in diagnosing a disease called Lactic Acidosis (1).

In this work, we utilized NAD (nicotinamide adenine dinucleotide)-dependent lactate dehydrogenase (LDH, EC. 1.1.1.27), which catalyses oxidation of L-lactate to pyruvate and simultaneously reduces NAD^+ to NADH. As a matrix for immobilization of LDH on the glassy carbon electrode, multiwalled carbon nanotubes (MWCNTs) were used, due to their unique electronic and mechanical properties. MWCNTs have been modified by polyelectrolyte-poly(diallyldimethylammonium chloride) (PDDA) to provide competent interaction between enzyme molecule and the nanostructured matrix. Negatively charged protein can electrostatically react with positively charged atoms of nitrogen located on PDDA modified MWCNTs. Owing to modification, the stable and colloidal solution of nanotubes was obtained (2,3).

To examine biosensor for electrocatalytic properties of lactate oxidation in different pH (7.0 and 8.0) of 0.1 M phosphate buffer solution, cyclic voltammetry and amperometry were employed. Current densities were increased during successive additions of lactate. Using the Lineweaver-Burk plot, parameters of biosensor were determined. In pH 8.0 our biocomposite MWCNTs/PDDA-LDH is described by high sensitivity (20.17 **µ**A cm^{-2} mM^{-1}), good linearity range (0.50-1.75 mM), low Michaelis-Menten constant (1.42 mM) and detection limit (0.79 **µ**M). To characterize biosensor, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and infrared spectroscopy (FTIR) were applied.

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P14. **Gated Electron Transfer Reactions of Truncated Hemoglobin from *Bacillus subtilis* Differently Orientated on SAM-modified Electrodes**

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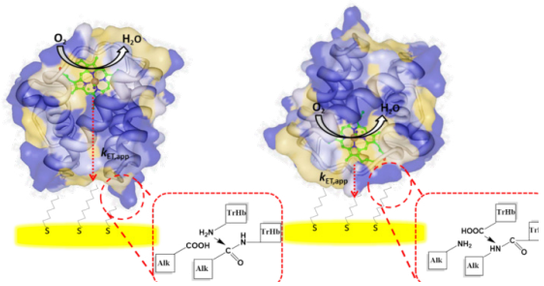

Scheme: Schematic representation of the electrode modification by trHb-Bs covalently attached to (left panel) COOH- and (right panel) NH_2- terminated alkanethiol SAMs on gold.

Electron transfer (ET) reactions of truncated hemoglobin from *Bacillus subtilis* (trHb-*Bs*) are suggested to be implicated in biological redox signaling and actuating processes that may be used in artificial environment sensing bioelectronic devices. Here, kinetics of ET in trHb-*Bs* covalently attached via its surface amino acid residues either to COOH- or NH_2-terminated $(CH_2)_{2–16}$ alkanethiol SAM assembled on gold are shown to depend on the alkanethiol length and functionalization, not being limited by electron tunneling through the SAMs but gated by ET preceding reactions due to conformational changes in the heme active site/at the interface. ET gating was sensitive to the properties of SAMs that trHb-*Bs* interacted with. The ET rate constant k_s for a $1e^-/H^+$ reaction between the SAM-modified electrode and heme of trHb-*Bs* was 789 and 110 s^{-1} after extrapolation to a zero length SAM, while the formal redox potential shifted 142 and 31 mV, for NH_2- and COOH-terminated SAMs, respectively. Such domain-specific sensitivity and responsivity of redox reactions in trHb-*Bs* may be of immediate biological relevance and suggest the existence of bioelectronics regulative mechanisms of ET proceeding in vivo at the protein–protein charged interfaces that modulate the protein reactivity in biological redox signaling and actuating events.

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P15. **Modifying the liquid/liquid interface with mesoporous silica electrochemically generated**

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The ever-growing family of mesoporous silica materials continues to stimulate the interest in various fields of chemistry, with a wide range of potential applications in catalysis, separation, adsorption, coatings, and nowadays in electrochemistry due to their unique properties and functionalities that can be effectively exploited (1). Mesoporous silica materials are usually obtained by a two-step sol-gel process: (i) silica precursors (tetraethoxysilane, organically modified silanes, or a mix of them) are hydrolysed in the presence of surfactant; (ii) silica is then condensed around a surfactant template. This step can be controlled electrochemically at the liquid-liquid interface (2). Silica condensation is initiated by the transfer of template ion cetyltrimethylammonium (CTA^+) from the organic phase to the aqueous phase containing hydrolysed tetraethoxysilane. In previous studies, it has been shown that silica electrogenerated at liquid-liquid micro-interface arrays is mesoporous in the right experimental conditions (3). Ion transfer across the interface is influenced differently by the presence of mesoporous silica deposits (4), suggesting that sieving properties might be achieved.
In this work, the miniaturized interface between two immiscible electrolyte solutions was modified with a mesoporous silica material. Herein chemical functions were introduced to the mesoporous silica by co-condensation of organosilanes followed by oxidation of thiol-functionalized mesoporous silica or by cycloaddition of azide-functionalized silica with a selected alkyne (1-dimethylamino-2-propyne, “click chemistry” reaction). The functionalized mesoporous silica deposited at the micro-interface was then characterized by cyclic voltammetry of model cations (tetraalkylammonium) and one anion (4-octylbenzene sulfonate), with the aim of developing a new class of electrochemical sensors.

Acknowledgements: The authors are grateful to the Agence Nationale de la Recherche (Hyperion project ANR-14-CE04-0002-01) for financial support.

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P16. **The Practical Manufacture and Use of Different Electrodeposited Polymers as Immobilization Interfaces for Affinity Based Biosensors**

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Over the years many publications have reported the use of electrodeposited conducting and non-conducting polymers as functional nanostructured surfaces to immobilize enzymes and other proteins, such as antibodies. Most of these reports are biosensor related, where the protein used is the bio-recognition agent to introduce specificity into the biosensor produced and the electrodeposited polymer acts as a surface functionalization agent.
ELISHA Systems Ltd is a spin-out company coming from an EU project of the same name, based in the University of Leeds. In the last 8 years many different aspects of electrodeposited polymers have been explored, including type of deposition, electronic state and reproducibility, with the emphasis always being on affinity based biosensors (1-3).
In this talk practical experiences will be shared to show that conducting polymer layers have much more influence on biosensor performance than just a chemical functionalization layer to enable immobilization of proteins. Also the chemical and physical characteristics of the conducting polymer produced are important in the choice of which polymer to choose for particular applications. Linked to these aspects, the choice of the base electrodes used, the electrode materials, the counter ions used and the method of electrochemical deposition influences the eventual nanostructure, morphology and surface chemistry of the polymer surfaces produced.
In addition to conductive polymers, electrodeposited non-conducting polymer surfaces will also be discussed and in particular, polytyramine which has found uses in the immobilization of antibodies and peptide aptamers to fabricate affinity based biosensors. The talk will be illustrated with experimental data from a range of different biosensors and polymer systems to give some practical information for further research efforts.

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P17. **PLGA microspheres with incorporated gold nanoparticles - physicochemical and biological characterization of the targeted drug delivery system**

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Polymeric colloidal structures have received considerable interest in recent years due to their unique optical, mechanical and catalytic properties. They have found several applications within the field of chemical analysis, catalysis, as well as medical diagnostics and therapy (1). Particular attention is being paid to medical applications because polymeric colloidal particles may be used at the same time as drug carriers and contrast agents in non-invasive imaging methods (2).
The aim of the project was to fabricate biodegradable PLGA (poly(lactic-co-glycolic acid)) microspheres modified with radioactive gold nanoparticles (^{198}Au) and to examine their applicability as drug carriers. These hybrid structures consist of PLGA polymer (in the form of spherical beads), gold nanoparticles (immobilized on the surface of the microspheres) and thiolated polyethylene glycol with folic acid group, adsorbed on the surface of gold.
The microcarriers (with radioactive or stable gold nanoparticles) were characterized with a number of physicochemical techniques which provided information on their structure, surface morphology and chemical composition (volume and surface) as well as the amount of deposited gold or radiochemical activity.
The second part of the project involved biological characterization of the resulting microcarriers (including those labeled with gold-198). We have used confocal microscopy to investigate penetration of the carriers into tumor cells (MCF-7 cell culture). The cytotoxicity of the carriers after loading with doxorubicin was examined using an MTT assay. These studies have shown that the hybrid particles are promising as smart drug carriers.

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P18. **The use and optimization of Nanobodies in reagentless immunosensors**

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Immunosensors have the potential to revolutionize clinical practice by enabling th point of care diagnostics of a wide range of biomarkers. Within this field, there is currently a movement towards antibody mimetics as well as monoclonal antibody derived reagents. This is driven by the need and desire to lower costs, improve efficacy and reduce reliance on animals. In my research I have used nanobody based sensors which were interrogated electrochemically; nanobodies are recombinant binding proteins initially derived from camelid heavy-chain only antibodies[1,2]. These sensors have highlighted potential pitfalls when using "off-the-shelf" antibody mimetics in reagentless impedimetric immunosensors. As well as identifying these issues, the work allowed for molecular engineering to enhance their capabilities.
By introducing oriented peptide spacers, not only has the degree of receptor orientation been enhanced but also, the spacing from the electrode surface has been optimized and has allowed the bioreceptor to be positioned within specific electrochemical double layers. This has resulted in greater signal generation in a novel sensor system and generated fresh insight to the role the electrode interface plays in signal generation in impedimetric biosensors.
It is hoped that this work may contribute and inform further development of electrochemical biosensors fabricated using other non-antibody binding receptors and may assist in the acceleration of research in the field.

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P19. **Tailored building blocks for molecular imprinting**

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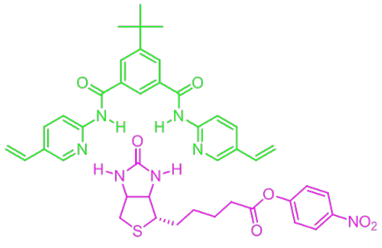
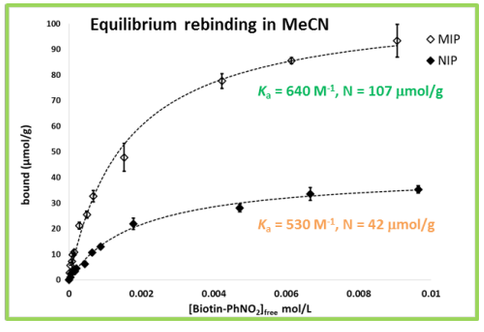
Molecular imprinting is an extremely versatile and attractive method for preparing synthetic receptors with antibody-like properties for a range of bioanalytical targets. The majority of reported molecularly imprinted polymers (MIPs) are based on copolymers of only two monomers, methacrylic acid as the "functional" monomer and ethylene glycol dimethacrylate as the matrix-forming cross-linking monomer. Although such systems give "working" MIPs, their use is dogged by their low capacities and high levels of non-specific binding. In our work, we try to circumvent such issues through tailored design.
We have long been engaged in designing and synthesizing novel binding monomers tailored towards particular analyte target groups, e.g. vitamins(1), antibiotics(2) and peptides.(3) These *stoichiometric* non-covalently imprinted materials are useful for the selective extraction of such compound classes from food, environmental and biological samples. Currently, we are extending this synthetic effort to consider *all* the building blocks in imprinted systems.(4)



Pre-polymerisation biotin-monomer complex
[K_a ($CDCl_3$) = 1220 M^{-1}]



Here, we would like to present our recent work on binding monomers targeting barbiturates and biotin (see above), together with strategies for the integration of these systems into biosensors.

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P20. **Differential pulse voltammetry (DPV) measurement of surface coverages for modified electrodes**

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The traditional way for determining the surface coverages (Γ) of attached redox molecules for modified electrodes is by estimating the charges under the oxidation and reduction peaks in cyclic voltammetry[1]. However conventional cyclic voltammetry (CV) is not very sensitive for low coverages of surface modified species. In contrast, differential pulse voltammetry (DPV) is more sensitive but it is not usually used for extracting the surface coverages[2, 3]. Here, we provide a method to extract the surface coverages from DPV and the application of our model to the analysis of DPVs for covalently attached monolayers of anthraquinone (AQ) on glassy carbon (GC) electrodes.

Our approach makes use of an additional external uncompensated resistance (R_u) in the DPV cell circuit together with a suitable set of DPV parameters. Subsequently, the Γ_{DPV} of covalently attached AQ at a suitable R_u can be determined by integrating the area under the DPV oxidation waves after performing a background subtraction. The DPV for the attached species was simulated using software in MATLAB in order to validate the experimental approach. Parameters for the MATLAB simulation such as electrode kinetics (k_s and α), uncompensated solution resistance (R_s) and double layer capacitance (C_{dl}) were obtained from cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements made on the modified electrodes. Excellent agreement was obtained between the experimental DPV and the simulation.

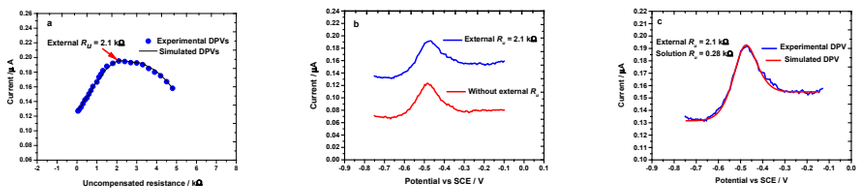

Figure 1: (a) A plot of DPVs currents *vs* external R_u. (b) DPVs for without external R_u (red) and with external R_u = 2.1 kΩ (blue).(c) DPVs for simulated (red) and experimental (blue) dataat external R_u = 2.1 kΩ.

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P21. **Chemical sensor for selective determination of gluten proteins using molecularly imprinted polymers (MIPs) as recognition units**

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Gluten is a mixture of plant proteins that are components of certain food products causing diseases, such as celiac sprue, allergy as well as gluten sensitivity. These diseases are dangerous, especially for children. Gluten enteropathy, also known as the celiac disease or celiac sprue, after hypolactasia, is the second most common food intolerance. This autoimmune disease of small intestine is caused by the ingestion of gluten proteins from widely prevalent food sources, such as wheat, rye, and barley. Exposure to gluten induces an inflammatory response leading to destruction of the villous structure of the intestine.(1)

The primary epitope in wheat gluten, which binds to IgE antibody, was determined as amino acid sequence PQQPFPQQ. Moreover, it was proved that the same octapeptide sequence is present in such fractions as omega-gliadin in wheat, omega-secalin in rye, and C hordein in barley. This epitope is responsible for several allergenic reactions.(2)

In our work, we devised and fabricated dedicated chemical sensor for selective determination of gluten epitope, PQQPFPQQ, using molecularly imprinted polymer (MIP) films as a recognition unit of the chemical sensor. The MIP film was prepared by electrochemical polymerization of bis(bithiophene) derivatives, bearing either cytosine or carboxylic acid substituent, in the presence of the template and a cross-linker. After deposition, the template was extracted from the polymer film. Subsequently, the film composition was characterized by X-ray photoelectron spectroscopy (XPS) as well as its morphology and thickness were studied by scanning electron (SEM) and atomic force (AFM) microscopy. Finally, analytical parameters of the devised chemosensor for epitope detection were evaluated.

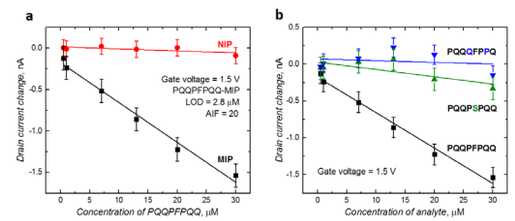

Figure 1. Preliminary results of gluten epitope in buffer (pH≈7) determination using extended-gate field-effect transistors (EG-FETs) as transducers. (a) Calibration curves for the gluten epitope on the MIP and NIP film-coated EG-FETs. (b) Comparison of calibration curves of similar epitopes on MIP film-coated EG-FET.

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P22. **Immobilization of Lactate Oxidase on Electrochemically Reduced Graphene Oxide-Carbon Nanotubes Hybrid System for Lactate Biosensing**

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Lactate oxidase (LOx) (EC 1.1.3.2) has stimulated interest as bio-recognition element for lactate sensing during the last years. LOx belongs to the family of flavin mononucleotide-dependent oxidizing enzymes and catalyzes the oxidation of L-lactate to pyruvate (1). To facilitate electron transfer between the enzyme molecule and electrode surface carbon nanomaterials such as: multi-walled carbon nanotubes (MWCNTs) and graphene are used. They exhibit favourable mechanical, electronic, thermal, and structural properties (2). Additionally, graphene oxide (GO), which can be easily converted to graphene, shows a unique capability to form stable aqueous dispersions. Moreover, it is highly bio-compatible and has good electrocatalytic properties. It was reported previously that it is possible to form a water dispersion of GO-MWCNTs hybrid material by non-covalent π-π stacking interactions (3). However, the aliphatic sp^3 hybridized domain results in the insulating properties of GO. Therefore for improving the conductivity, graphene oxide can be reduced to graphene either by chemical, thermal or electrochemical methods.
In presented work we constructed lactate bioelectrocatalytic system by immobilization of the lactate oxidase enzyme onto ERGO/4-(pyrrole-1-yl) benzoic acid (PyBA) modified MWCNTs hybrid system. Modification of MWCNTs with PyBA improves effective transfer of electrons between the active center of the enzyme molecule (LOx) and the electrode surface. Carboxyl functional groups from PyBA form stable covalent amide linkages with amine groups from the enzyme molecule, which significantly improves stability of our ERGO/MWCNTs/PyBA integrated system (4). Faciliation of direct electron transfer between the LOx protein and the glassy carbon electrode by the ERGO/MWCNTs/PyBA system was confirmed. The immobilized enzyme revealed a pair of well-defined and reversible redox peaks. The formal potential taken by potential values of the E_a and E_c in scan rate 25 mV/s was -0.444 V vs. Ag/AgCl in 0.1 M phosphate buffer solution pH=7.0. The apparent Michaelis-Menten constant was calculated by the electrochemical version of the Lineweaver-Burk plot and was found to be K_M=8.25 mM, implying the high enzymatic activity and affinity of immobilized enzyme for lactate.
These findings have established the direct electrochemistry of the LOx protein, revealing its potential application as a biosensor for quantitative detection of lactates in real samples.

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P23. **DNA Aptamers As Sensing Layers for Detection of Potassium Ions**

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Potassium is one of key elements that plays a significant role e.g. in the maintenance of nerve stimulation, enzyme activation and regulation of membrane potential (1). Abnormal level of K^+ ions might lead to various diseases including diabetes, kidney's and stroke (2), thus, the development of a sensitive method for monitoring of K^+ concentration is of special importance. For the clinical detection of potassium ions, ion-selective electrodes (ISE) have been frequently employed, with an electroactive membrane containing ionophores such as valinomycin (3) and ion-carriers including macrocyclic crown ethers (4).
Since 1990s a great interest was given to the application of nucleic acids including aptamers as sensing elements, as they exhibit catalytic and receptor role. One of the first assays containing aptamer recognition layer was designed by O'Sullivan and dedicated for determination of K^+ ions (5). Since then, aptamer probes of different length and nucleic base content were utilized for the elaboration of potassium aptasensors (1,2,6).
Herein, an electrochemical sensor for K+ ions was developed with the use of DNA aptamers of various sequences as recognition layers. The assay was formed by tethering of thiolated aptamer probes to gold disk electrode via Au - S bond. Potassium – aptamer binding was analyzed in presence of redox indicators – methylene blue (MB), AQMS and Na4Fe(CN)6 with the application of voltammetric techniques. The studies revealed that 15-mer thrombin binding aptamer (TBA) exhibited highest affinity towards K+ with K_d = 1.13 · 10-6 M. The proposed aptasensor demonstrated linear response towards potassium within the range from 10-8 to 10-5 M with a detection limit of 2.31 · 10-9 M and good selectivity using MB as electroactive indicator.

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P24. **Doxorubicin Loading and Releasing from Liposomes Decorated with Hydrophobic Magnetic Nanoparticles**

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Well-controlled delivery of substances to cells is highly desirable. Modern therapies demand that such drug-delivery systems will carry as much medicine as possible, will be nontoxic and also will facilitate diagnosis. We designed liposomes that are believed to meet all of these requirements. We used magnetic nanoparticles (MNP) in such liposomes as a prospective vector in magnetically-driven targeted drug delivery.

MNP of Fe_3O_4 were synthesized with coprecipitation method from inorganic precursors. Their surface was modified with oleic acid rendering MNPs hydrophobic. To characterise these MNP we used several techniques, incuding SEM, EDS, TEM, SQUID, DLS and TG. Such obtained small (4-10 nm) hydrophobic MNPs were incorporated in the bilayer lipid membrane of liposomes. Liposomes were prepared by mixing two nonpolar lipids – DOPC and DPPC with an appropriate amount of nanoparticles in chloroform. After evaporation of organic solvent, resultant lipid film was hydrated with buffer and then the magnetoliposomes were formed by extrusion or sonication. TEM pictures showed that nanoparticles tend to aggregate inside the lipid bilayer.

Next we encapsulated doxorubicin, the anticancer drug, inside such magnetoliposomes via passive or pH-gradient (remote) loading. Doxorubicin release was effected by liposome rupture either with increasing temperature increase above the lipid phase-transition temperature, addition of surfactant or using alternating magnetic field. The amount of free drug in suspension was measured using electrochemical and spectroscopic techniques (see Figure 1). We believe these liposomes could be useful in anticancer therapies.

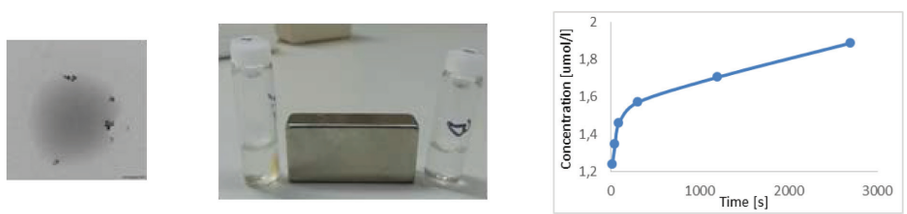

Figure 1 – Magnetoliposome (left), aggregation of magnetoliposomes near permanent magnet (middle), releasing of DOX caused by alternating magnetic field (right)

P25. **Flexible enzymatic fuel cell with solid-state electrolyte**

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Progress in nanotechnology has created new directions in the design of nanoscale electronic devices suitable for various applications, e.g. in medicine or environmental science. To keep such miniaturized electronic devices operating for long periods of time, there is a need of low power sources. Although Enzymatic Fuel Cells (EFC) provide great selectivity of processes occurring at the electrodes, possibility of miniaturization and low overpotential of redox reactions, the available EFCs still suffer from insufficient power densities and vulnerability on high currents load, e.g. during switching on/off the powered devices (1). Therefore, similar to conventional electrolyte batteries, enzymatic fuel cell need to be stacked in order to boost their single cell voltage up to practical level. Here we report a laminated stack of EFCs that is composed of bioanode fabrics for fructose oxidation hydrogel containing electrolyte and fuel, and O_2 – diffusion biocathode fabrics. The anode and cathode fabrics were prepared by modifying fructose dehydrogenase and laccase, respectively, on carbon nanotubes – decorated carbon cloth. Solid state electrolyte based on polymethacrylate derivatives was used to decrease the problem of mechanical instability of modified electrodes working under solution flow condition. Also, such architecture enables diffusion of oxygen from air directly to electrode surface, which decreases diffusion limitation of cathode (2).

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P26. **Bioelectrocatalysis in redox-active hydrogel films – Solvent effect on redox potential**

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The conversion of small molecules like H_2 and CO_2 with the use of catalysts is central for renewable energy conversion to face climate change and fossil fuel depletion. Currently, catalysts for technological energy conversion are mostly based on rare and expensive metals, but it has been proposed that molecular catalysts and even bio-catalysts could be used instead. A major challenge to employ such catalysts for the conversion of small molecules is their fragility and sensitivity towards oxygen. To overcome these problems, redox hydrogel films were introduced to stabilize enzymes into the polymer matrix and protect them from deactivating molecules (*1- 3)*.

Beside the desired properties for catalyst protection, the redox hydrogel has to be optimized in terms of redox potential and electron transfer to achieve high current densities at low overpotential. Using viologen-modified polymers we observed a shift in potential during biocatalytic processes in form of a hysteresis in the catalytic current during cyclic voltammetry. Such hysteresis indicates a shift in redox potential of the redox polymer and hence a drift from the ideal polymer properties for a given application. We demonstrate that this hysteresis is induced through hydrogel solvation/desolvation and is affected by the counter ions. The desolvation of the redox moieties increases their interactions with the polymer backbone and consequently affects their electron density and redox potential. The Hofmeister series was used to explain the effect of the counter ion on potential shift. This study illustrate the importance of hydrogel solvation in bioelectrocatalytic processes.

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P27. **Bioelectrocatalytic Glucose Oxidation on Electrochemically and Chemically Reduced Graphene Oxide Noncovalently Modified with Tetrathiafulvalene**

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Graphene, a two-dimensional nanomaterial, constitutes a new carbon comprising layers of carbon atoms arranged in six-membered rings (1). It has attracted intense attention due to its unique electronic, thermal and mechanical properties. Graphene possesses a high ratio of surface area, a good conductivity and mechanical properties comparable with (or even better) than carbon nanotubes. Owing to its inert chemical property and highly hydrophobic surface, graphene is considered as an ideal support for redox mediators via π-π stacking interactions (2).

Many chemical methods have been developed for the preparation of graphene, such as epitaxial growth on silicon carbide and chemical reduction of graphene oxide (GO). As the oxidized form of graphene, GO could be easily obtained via a simple chemical processing of graphite. GO contains a range of reactive oxygen containing functional groups, which endows it water solubility and possibility for further biological applications. However, excess of oxygen may break the sp^2 structure of graphene, as a result deteriorate its conductivity.

In the present work, we have exploited unique characteristics of reduced graphene oxide (obtained by electrochemical treatments (ERGO) and chemical treatments with hydrazine (CRGO)) to construct the efficient anodic glucose oxidase based bioelectrocatalytic systems of potential utility for biofuel cells and biosensors. A noncovalent modification method of ERGO and CRGO conducting support with a mediator, tetrathiafulvalene (TTF), and the bioelectrocatalytic activities of ERGO-TTF and CRGO-TTF composites with immobilized glucose oxidase toward the oxidation of glucose have been demonstrated.

The presence of TTF is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode (3). TTF and its derivatives constitute a group of redox molecules that were successfully used as redox mediators in enzyme electrochemistry. Due to the existence of hydrophilic cation-exchange domains within Nafion deposits on graphene, capable of retaining soluble TTF^+, the overall stability of the bioelectrocatalytic film has increased. As before, reduced graphene oxide have supported transport of electrons within the bio-electrocatalytic system. On the whole, combination of TTF-graphene and glucose oxidase within the film has produced a catalytic system capable of effective oxidation of glucose in 0.1 M phosphate buffer (pH=8.0). The formation, morphology, and electrocatalytic reactivity of our bioelectrocatalytic films containing of TTF-modified graphene were examined using cyclic voltammetry, amperometry, FTIR spectroscopy, transmission and scanning electron microscopy.

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P28. **Correlated topographical sensing using self-sensing cantilever Atomic Force microscopy**

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Advances in micro-, nano-, and biotechnology put increasing demands on nano-scale microscopy and characterization. Atomic force microscopy (AFM) is one of the highest resolution microscopy methods used in this area. In this work, we developed a new platform of AFM sensors and a modular AFM system, which significantly increases the performance of AFM and make it suitable for a much broader range of applications from material to life sciences.
While traditional AFMs using optical detection of the cantilever sensor, yield very high resolution images, they show a lack in stability, are difficult to automate, and integration with other analysis techniques is limited due to the required optical components. In this work we remove these limitations for a large area of attractive AFM-applications and allowing for the combination with other techniques performing correlated microscopy and sensing.
Used basic cantilevers are in the range of 80-300µm in length, 30-100µm in width and of different thickness. They are equipped with 4 piezo-resistors in Wheatstone bridge formation at the cantilever basis to detect the surface stress caused by cantilever bending due to topographical changes. From the basic cantilevers highly specified sensing devices can be fabricated using Focused Electron Beam Induced Deposition (FEBID). Implementation of heating loops for driving the cantilever in none contact dynamic mode allows independent actuation and readout from single cantilevers in array configuration.
This novel cantilevers are on the one hand implemented to a commercial bio-AFM for topographical sensing of biological samples in dry state and liquid and are on the other hand used with a newly developed modular AFM platform for correlated microscopy.

P29. **Deposition of phenothiazine modified polymers based on electrochemically induced crosslinking for wiring of enzymes**

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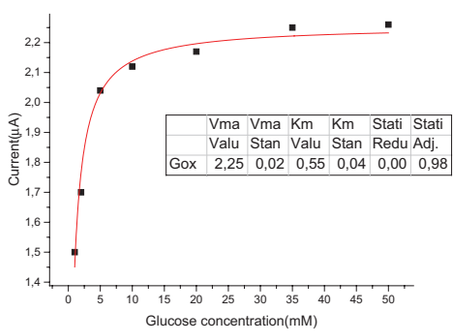
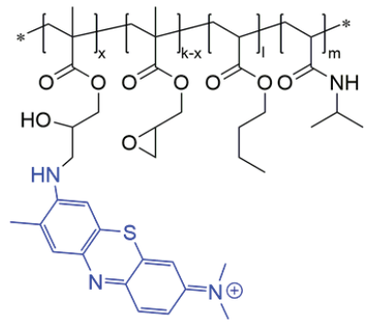
A major advantage of electrochemically induced deposition of redox polymer for the electrical wiring of enzymes over more conventional methods (e.g drop coating) is the possibility to form active films on small electrode surfaces for the use in miniaturized electrochemical cells with volumes of 50–100 µl. Therefore, the development of new strategies for a non-manual immobilization of redox polymers is of particular interest for the miniaturization of amperometric biosensors.
Here, we report on a new method based on the pulsed immobilization of different enzymes via an electrochemically induced crosslinking process leading to the formation of dense hydrogel networks entrapping the enzymes. Moreover, by varying the conditions during the electrochemically induced crosslinking process, i.e. number of potential pulses and/or pulse duration, this method enables to control the thickness of the deposited polymer layers.
The polymers bear phenothiazine-based low-potential redox mediators that are capable of shuttling the electrons between the enzyme and the electrode. These low potential redox polymers in combination with different enzymes (such as cellobiose dehydrogenase (CDH); FAD-dependent glucose dehydrogenase (FAD-GDH); and glucose oxidase (GOX)), were successfully used for the amperometric detection of glucose and as bioanodes in glucose/O_2 biofuel cells.



	Vma Valu	Vma Stan	Km Valu	Km Stan	Stati Redu	Stati Adj.
Gox	2,25	0,02	0,55	0,04	0,00	0,98



P30. **A new analytical platform for biomolecules: Nanoparticle size-shifted assay using synthetic binding proteins**

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Detection of biomolecules or small molecules (e.g. pesticides) usually involves labelling analytes with chromophores, fluorophores or radiolabels, which is time-consuming and expensive. Also, these molecules can interfere with analytes and their molecular interactions, which lead to false negatives or positives. Hence, a label-free analytical platform is an alternative option for biomolecules detection or drug screening assays. From a theoretical perspective, it is possible to adapt the biosensor concept into a new label-free assay system. The proposed analytical platform uses engineered binding proteins, "Adhirons", instead of antibodies as the biorecognition element within a system, combined with a transduction process that is based on dynamic light scattering (DLS). Adhirons exhibit the promising property of being an effective bioreceptor with similar specificity to antibodies but are more easily produced and stable thermodynamically and chemically(1). The principle of the new platform is to use Adhirons functionalised gold nanoparticles as bioreceptors. Detection is based on size-shift of the nanoparticles, which can be detected using DLS, after binding of the analyte occurs. The possibility of this platform was tested with glutathione-S-transferase (GST) binder Adhirons clones A2, A3 and H6, which is suggested that the system is possible for a dimer (GST). Ongoing experiments are being performed for testing the system with a monomeric target molecule, which is myoglobin – used as a model protein analyte, but it is also a biomarker of myocardial infarction and generally for muscle damage.

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P31. **Hybrid Nanomaterials for Oxygen Reduction and its Application in Hybrid Biofuel Cell**

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We present the results of our studies on different hybrid nanomaterials useful for the electrodes in hybrid biofuel cell and full biofuel cells. The best substrates for the cathode were carbon paper (CP) Toray Teflon Treated TPG-H-120. We employed laccase or bilirubin oxidase as the biocatalyst catalyzing 4-electron reduction of oxygen to water and different carbon nanomaterials for the immobilization of enzyme in its active form. Multi walled carbon nanotubes increased the working surface of electrode, improved conductivity and provided direct electron transfer between the enzyme and the electrode (1, 2).
Zinc disc was employed as the anode in hybrid biofuel cell. In the full biofuel cell fructose dehydrogenase (FDH) was employed as the anode biocatalyst. Parameters of the biofuel cell were evaluated under flowing solution conditions. A self-powered sensing system for neurotransmitters was constructed with the hybrid biofuel cell as the powering unit.

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P32. **Determination of Influence of a New Bacteriocin-like peptide BacSp222 on a Model Biological Membrane by Chronocoulometry, AFM and PM-IRRAS**

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The secondary structure and orientation of newly synthesized bacteriocin-like antimicrobial peptide BacSp222 adsorbed in a model membrane were investigated. Chronocoulometry, atomic force microscopy (AFM) and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) combined with electrochemical methods were utilized to characterize the mechanism of interaction between BacSp222 and planar phospholipid bilayer comprised of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) deposited at a single crystal gold electrode Au(111). BacSp222 is a unique peptide that possess features characteristic both for bacteriocins and virulence factors. The bacteriocin is a 50 amino acid linear peptide formylated on N-terminus, produced and excreted by *S. pseudintermedius* strain 222 isolated from dog skin lesions. BacSp222 is able to kill Gram-positive bacteria but is inactive against Gram-negative bacteria and fungi. Electrochemical methods were employed to study the stability of the model membrane while PM-IRRAS was used to obtain information regarding the conformation and orientation of DMPC and BacSp222 within the membrane. Analysis of the PM-IRRAS spectra in the Amide I region showed that BacSp222 is predominantly α-helical, with β-turns and β-sheets components are also present. In wide potential range, BacSp222 molecules are inserted almost perpendicular to electrode normal. AFM imaging showed significant change in the DMPC bilayer topography after BacSp222 adsorption.

P33. **Surface modification by Self-Assembled Monolayers of fluorescent dyes**

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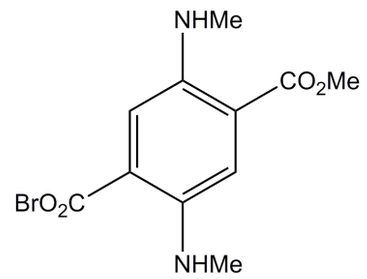
Surfaces can be modified by self-assembly of organic molecules. Molecules are chemisorbed on the surface by "head groups", for which thiols or silanes are suitable for gold or glass surfaces (1).
Here we aim to assemble diaminoterephthalic acid on a gold surface in mixed self-assembled monolayers. Diaminoterephthalic acid derivatives have been synthesized as fluorescent dyes by Wallisch and Christoffers (2). Some derivatives are turn-on probes, e.g. they emit fluorescence only when bound to an effector (3) which make the distinction of reacted vs. unreacted dye very simple.
Dyes based on diaminoterephthalic acid can react with the amino group of amionoctanethiols that are assembled on the surface. Organization of the self-assembled monolayers prepared on this way can be observed by atomic force microscopy. Surface characterization can be obtained by common electrochemical methods such as cyclic voltammetry but also by a photoelectron spectroscopy and fluorescence spectroscopy. Dyes based on diaminoterephthals change their emission wavelength depending on the occupation of binding sites, so they can be used as scaffolds on the surface for attaching nanoparticles, π-electron-rich molecule or proteins.



Scheme 1. Fluorescence dyes based on diaminoterephthalic acid

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P34. **An Ultra-Sensitive Lipopolysaccharide Sensor Based on an Orientation-Specific Self-Assembled Monolayer and Toll-Like Receptor-4**

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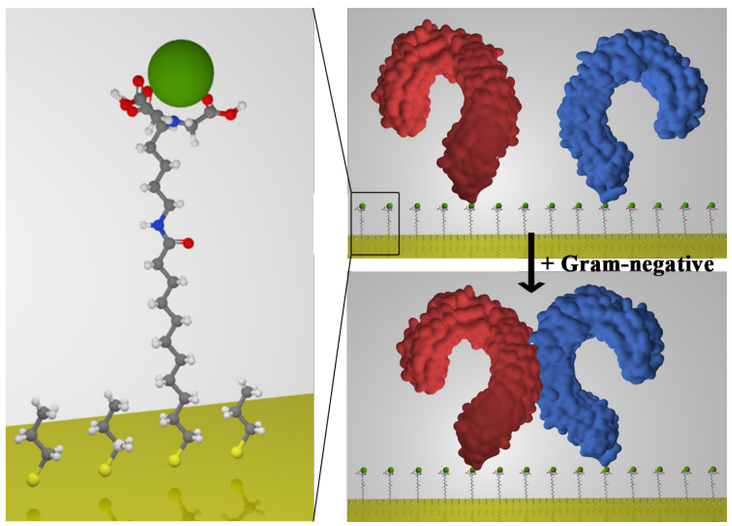
Infections affect millions of people each year, yet discerning their cause can take more than 24 hours. This delay between the presentation with symptoms and the ability to make an informed decision about treatment can have serious consequences. Developing a detection system based on the immune system offers the advantage of broad specificity, while still remaining pertinent to human health. In this work, human Toll-Like Receptor-4 (TLR-4), a protein responsible for detecting Gram-negative bacteria, was immobilized on a gold electrode via the tethering interaction of a modified self-assembled monolayer (mSAM). In response to varying concentrations of its target, the protein-electrode combination showed a logarithmically proportional increased resistance to charge transfer due to the formation of TLR-4 protein dimers. It also demonstrated excellent sensitivity to trace levels of Gram-negative bacteria, while remaining completely insensitive to both Gram-positive bacterial and viral challenges. Further characterization of our mSAM has revealed that maintaining an orientation mimicking TLR-4's role in a cellular context resulted in the most responsive sensor.



P35. **Multiscale design of porous carbon electrodes for efficient enzymatic fuel cells and bioreactors**

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Carbon-based materials are largely used in electrochemistry, notably in the domains of electroanalysis and bioelectrochemistry. Versatility of allotropic modifications and rich surface chemistry, together with well-established fabrication methods, make carbon-based electrodes ideal for enzyme immobilization. The efficiency of bioelectrodes is related to the quantity of electrically-wired enzymes, which is usually directly proportional to the electroactive surface area. Carbon nanotubes (CNT) exhibit large surface areas and have various active sites on their ends and wall defects allowing effective enzymes adsorption. Numerous examples of carbon nanotubes enhancing an enzymatic response have been shown thus leading to increased current density.[1] However, in case of the most active enzymes operating at relatively low substrate concentration, the current becomes quickly limited by the substrate mass-transfer inside the biohybrid film.[2] This limitation can be overcome by proper design of the electrodes at the macroscale.

Here we report the development of large-scale electrodes based on carbon felt decorated with CNT. Nanostructuration allowed to enhance the response of immobilized enzymes in cases of both direct and mediated electron transfer and the open structure of carbon felt promoted unobstructed diffusion inside the electrode. Developed bioelectrodes were tested for two distinct applications that require large area electrodes with high enzyme loading: enzymatic electrosynthesis and enzymatic fuel cells.

Carbon felt modified with CNT was used for the immobilization of D-sorbitol dehydrogenase into sol-gel silica film which contributed to the improvement of the enzyme stability. Obtained biohybrid electrode was evaluated in a specially constructed flow-through bioreactor for the regio-selective bioconversion of D-sorbitol to D-fructose. The bioreactor was able to continuously operate during two weeks while producing D-fructose at a rate of 1.65 mg day^{-1} cm^{-3}.

Secondly, carbon felt decorated with CNT was employed in H_2/O_2 enzymatic fuel cell based on hydrogenase and bilirubin oxidase. Deposited CNT allowed to increase the bioelectrode active surface and the enzymatic current by 1.5 order of magnitude. The geometry of the bioelectrodes was optimized in order to maximize the reagents flux in the conditions of convection induced by gas sparging.

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P36. **Covalent immobilization of engineered Cellobiose Dehydrogenase from *Myriococcum thermophilum* at carbon-based electrodes**

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This study suggests a new approach for the construction of a stable glucose biosensor based on the covalent immobilisation of Cellobiose Dehydrogenase from *Myriococcum thermophilum* (*Mt*CDH) at carbon-based electrodes.

Cellobiose Dehydrogenase is a monomeric protein consisting of two domains containing two active sites: heme and FAD. Carbohydrates such as cellobiose, glucose and lactose are oxidised in the catalytic flavin domain, therefore electrons are transferred from FAD to heme, in a mobile cytochrome domain, through a mechanism known as internal electron transfer (IET) [1]. This interesting characteristic makes CDH a promising redox enzyme in the detection of carbohydrates, as it can give direct electron transfer (DET) without the need to add a mediator.

This project aims to develop new strategies for a stable immobilization of CDH, as well as other versatile redox enzymes, essential to the construction of biofuel cells, biosensors and implantable biodevices. To this purpose, a new method for the covalent immobilization of CDH to carbon electrodes has been studied, following a modular approach developed in a recent work of our group combining electrochemical and solid phase synthesis [2].

Glassy carbon electrodes (GC) and carbon nanotubes electrodes (GC/CNT) were modified with a maleimide group, which was chosen because it undergoes spontaneous reaction with cysteine at room temperature and neutral pH, making it an excellent choice for the selective attachment of cysteine-modified biomolecules. Therefore, CDH mutants genetically engineered to bear a free cysteine in different positions at the surface of the flavin domain were covalently attached to the electrodes, showing direct electron transfer in the presence of glucose.

Comparison experiments between the enzyme covalently immobilised at the electrodes surface and physically absorbed onto GC/CNT electrodes have been carried out, showing a better performance of the first electrodes as well as a greater stability of the immobilised biomolecule over the time.

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P37. **Voltammetric pH Nanosensor**

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There is a wide range of different pH sensors available, which can be voltammetric, amperometric or potentiometric in nature.(1) Potentiometric glass electrodes are the most common for pH measurement due to their high sensitivity and selectivity. Unfortunately they can suffer from “alkali errors”, instability and potential drift, that is why they have to be frequently calibrated prior to use. Although potentiometric pH sensors are useful and commercially available, they are not suitable for nanoscale measurements. We are focusing on a method using voltammetric pH sensing at carbon nanoelectrodes.

In this work a voltammetric nanosensor for wide pH range (2-12) is presented. It consists of pyrolytic carbon nanoelectrode obtained by chemical vapor deposition (CVD) of amorphous carbon inside a quartz nanopipette, and modified with 3,5-dimethoxy-4-hydroxybenzaldehydrazine (syringaldazine)(2) by adsorption. It exhibits a stable quasi-reversible cyclic voltammogram with nearly Nerstian pH-dependency of mid-peak potential. This sensor was applied as a scanning electrochemical microscopy (SECM) probe for pH mapping over a platinum sample microelectrode generating hydroxide ions (OH^-) in oxygen reduction reaction (ORR) at diffusion limiting rate in aerated phosphate buffered saline (PBS).

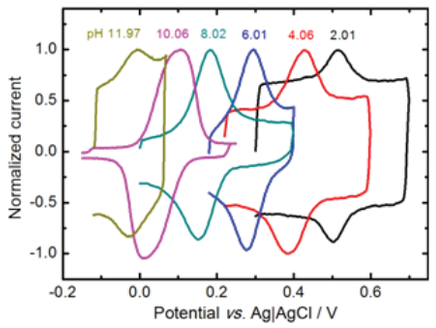

Fig 1. Selected cyclic voltammograms of carbon nanoelectrode with preadsorbed syringaldazine recorded in various pH (labeled) 0.1 M phosphate buffers. Current is normalized versus anodic peak value.

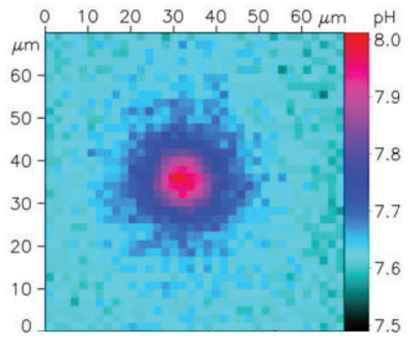

Fig 2. pH map recorded ca. 2.5 µm over a 10 µm diameter Pt disc electrode polarized at -0.8 V to reduce oxygen. Electrolyte: aerated phosphate buffer saline (pH 7.4).

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P38. **Electrospun indium tin oxide nanofibers as transparent electrode material for spectroelectrochemical analysis**

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Due to growing interest in chemo- and biosensors it is of utmost importance to develop materials and procedures to perform chemical analysis in cheaper, faster and more precise way. Employing simultaneously two methods of analysis such as electrochemistry and spectral analysis would enable more selective and time-efficient analysis. To fulfill this function the electrode material used has to be conductive and transparent. Furthermore to enhance the analytical response a high surface area is necessary e.g. by introducing porosity.

To reach this goal we produce indium tin oxide nanofibers by an electrospinning technique using a solution of mentioned inorganic salts and polyvinylpyrrolidone (PVP) in dimethylformamide and ethanol as precursors. Following this approach, nanofibers macroporous structure is obtained. Nanofibers diameter (ranging from 120 to 250 nm) was dependent on the voltage applied between the electrospinning needle and the electrode collector whereas the thickness of the deposited layer was proportional to the electrospinning time.

Crucial step of preparation of ITO nanofibers for analysis was a two-step calcination of electrospun nanofibers. After the deposition, they were put in oven in 500˚C to remove the PVP and to obtain pure indium tin oxide from indium tin hydroxide initially obtained during the electrospinning process. A second step of heating at 1000˚C under a nitrogen flow was performed to reconstitute the fibers and release tensions in crystalline structure. This latter step greatly enhanced the conductivity of the nanofibers. Moreover transparency measurements show that resulting surfaces can be suitable for spectroelectrochemical analysis.

To evaluate their electrochemical properties, nanofiber films have been tested using both fast- and slow- electron electrochemical probes, namely 1,1'dimethanolferrocene and ascorbic acid, respectively. A significant improvement of electrochemical signal with the film thickness has been observed with ascorbic acid as probe. Finally, spectroelectrochemical capabilities were investigated by deposition of prussian blue and subsequent measurement of the spectroscopic response to applied potential. It is important to note that ITO nanofibers have been prepared before using similar procedures but their electrochemical properties have not been tested[1,2].

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P39. **Ionic sensitivity of conducting polymer films and their suitability for constructing biomimetic membranes and sensors**

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Different methods for inducing [1-3] or suppressing [4] ionic sensitivity of the conducting polymer (CP) films doped with Metal Complexing Ligands (MCL) as well as Biologically Active Ligands (BL) will be presented. Both MCLs and BLs molecules introduced to CP layer as bulky doping anions are immobilized inside CP layer and preserve their chemical properties known from water chemistry. Similarly to ionophores, they form complexes inside CP membrane with selected cations only. The formation of the complex inside a polymer layer is necessary for inducing preferred ionic sensitivity of the CP membrane. Various methods for efficient sensitization of the CP-MCL and CP-BL films will be presented [1-3], and suitability of these films for constructing potentiometric sensors, biosensors or biomimetic membranes will be shown [5-6].

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P40. **Surface plasmon resonance as a promising analytical tool for study endo- and exocytosis**

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Understanding chemical secretion and uptake in cells through exocytosis and endocytosis is of great interest for researchers in medicine, biology and pharmaceutical industry. Exocytosis helps to shed light on processes such as transition of neuronal signals, cellular metabolism, immune cell functioning, cell-to-cell communication, the process of learning and memory, behavior and cognition, and development of degenerative disease like Alzheimer's and Parkinson's diseases (1-3). Drug screening and experiments aiming at unraveling the mechanisms of exocytosis/endocytosis regulation require methods that are capable of both rapid screening and providing quantitative information from a large number of cells. This is difficult to achieve with other currently used analytical techniques such as electrochemical and fluorescence microscopy.

With surface plasmon resonance (SPR) it is possible to measure the refractive index (RI) within cells with a great sensitivity, detecting changes as small as 10^{-6} refractive index units (4). Effects due to cell to cell variation are largely eliminated because the information is extracted simultaneously from a population of thousands of cells illuminated by the laser beam. In a hyphenated technique, electrochemical SPR (EC-SPR), the metallic layer (gold coated sensor chip) is used as a working electrode where oxidation or reduction occurs. The EC-SPR simultaneously measures minute changes in RI induced by vesicles migrating to, and fusing with the plasma membrane, and performs amperometric or voltammetric characterization of the released biomolecules, for quantifying and identification of the released species, respectively.

In the presented work, exocytosis and endocytosis of neurotransmitters are studied in PC12 cells cultured on gold coated SPR chips. During the experiments the cells need to attach to the metal surface and be able to withstand shear, therefore, conditions of culturing the PC12 cells were optimized. In addition, the uptake of nanoparticles and anti-cancer drugs by cells is also monitored. The SPR data is correlated with complimentary techniques like light and Raman microscopy. Furthermore, the cell characterization was in some instances supported by coherent scattering theory that provides the RI for particle containing samples.

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P41. **Hierarchical Materials for Molecular Recognition though Molecular Imprinting in Liquid Crystalline Media**

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We are exploring the use of liquid crystalline (LC) media in conjunction with molecular imprinting strategies for the development of hierarchical material architectures for use in a number of areas, *e.g.* in catalysis and theranostic applications (1). In the present study (2), the suitability of this concept for use with acrylate-based polymers is being examined. Imprinted polymers based upon methacrylic acid (MAA), 1,4-bis(acryloyl)piperazine (BAP) and bupivacaine were employed as functional monomer, crosslinker and template, respectively, were synthesized in lyotrophic liquid crystalline phases in a water/p-xylene and triton X-100 /water system on Au-coated quartz resonators. Polymer films were prepared using photochemical initiation condition, before being extensively washed using an optimized procedure to remove residual template. SEM studies reveal the polymer morphology was greatly influenced by the cylindrical LC phases affording well-oriented polymer structures in the nanometer scale with interconnected layers and channels extending to the micrometer scale. Infrared spectra verified the presence of the anticipated functionalities. Ligand recognition by the polymer films was assessed using the resonators in a quartz crystal microbalance (QCM, under FIA condition), and rebinding characteristics were even studied with the corresponding polymers synthesized in particle format. The imprinted polymers demonstrated a four-fold greater affinity for the template, bupivacaine, than non-imprinted material. The selectively of the materials was even examined using analogs of bupivacaine, ropivacaine and mepivacaine.

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P42. **Direct Electrochemistry of Bilirubin Oxidase Molecules at Carbon Nanoelectrode**

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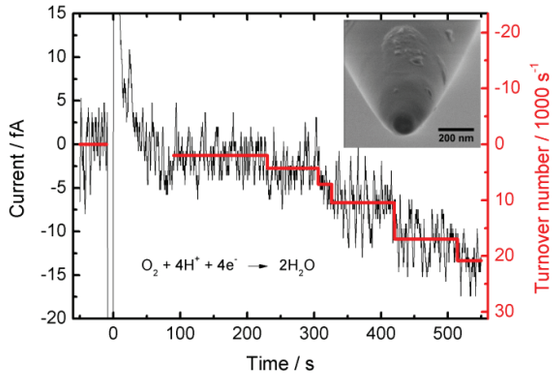
Macroscopic kinetics studies of ensembles of large number of enzyme molecules provide averaged parameters without activity distribution among individual biomolecules. Moreover, quantitative ensemble studies of enzymes require their precisely known concentration or surface coverage, which is problematic to evaluate due to impurities present in protein samples. Single molecule studies enable deeper insight into the details of enzymatically catalyzed processes. Although spectroscopic investigations of individual biocatalyst molecules have been performed,[1] direct electrochemistry of single redox enzyme molecules remains unexplored.[2-4]

In this study, we performed chronoamperometry on pyrolytic carbon nanoelectrode (CNE) in diluted solution of bilirubin oxidase (BOD) saturated with oxygen. Carbon materials are known to promote direct electron transfer to adsorbed BOD.[5] We observed staircase chronoamperometric response of negatively polarized CNE. We ascribe this behavior to adsorption of individual active BOD molecules.



Turnover number of direct electron transfer of BOD-catalyzed 4-electron oxygen reduction of single enzyme molecules appears to be one order of magnitude higher than the literature values determined by ensemble studies.[6] This suggest substantial content of inactive enzyme molecules and/or neutral impurities in samples of enzyme. Observed frequency of current steps, much lower than calculated from diffusion equations, can be caused by sluggish kinetics of BOD adsorption.

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P43. **Activity of Immobilized Enzymes on Electrochemically Reduced Graphene Oxide and in Macro- , Nanostructural Polyaniline Langmuir-Blodgett Films.**

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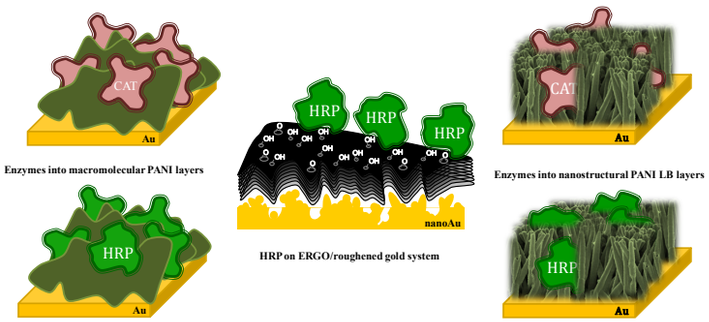
A major challenge for producing low cost biosensors based on macro- and nano-structured films is to control the molecular architectures a to preserve the catalytic activity of the immobilized biomolecules. The Langmuir-Blodgett (LB) method has long been used for the preparation of ultrathin films, offering the unique control over the film thickness and the molecular orientation.

In this study, enzymes such catalase (CAT) and horseradish peroxidase (HRP) has been incorporated into macromolecular polyaniline (PANI) matrix and LB layers of PANI nanotubes[1]. The biomolecules has been immobilized using physical adsorption, matrix entrapment and covalent bonds. The incorporation of biocatalyst molecules into polymer layers at the air-water interface was demonstrated with surface pressure isotherms. Finally Langmuir films were transferred on gold solid substrate[2].

The enzymes electroactivity of created biosystems was compared with respect to the HRP molecules attached to electrochemically reduced graphene oxide (GO) layers deposited on roughened gold[3]. Two types of GOs, partially reduced (ERGOP) and fully reduced (ERGOF) were used.

The biomolecules orientation[4] and their activity were investigate using infrared spectroscopy (PMIIRAS and IR microscopy) and electrochemical methods such as: cyclic voltammetry and chronoamperometry.



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P44. **Gold−Oxoborate Nanocomposites and Their Applications**

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A novel inorganic nanocomposite material, called BOA, which has the form of small building blocks composed of gold nanoparticles embedded in a polyoxoborate matrix, is presented. It is demonstrated that cotton wool decorated with the BOA nanocomposite displays strong antibacterial activity toward both Gram-positive and -negative bacteria strains. Importantly, the modified cotton does not release any toxic substances, and the bacteria are killed upon contact with the fibers coated with the BOA. Toxicity tests show that the nanocomposite−in spite of its antiseptic properties−is harmless for mammalian cells. The presented method of surface modification utilizes mild, environmentally friendly fabrication conditions. Thus, it offers a facile approach to obtain durable nontoxic antiseptic coatings for biomedical applications.
It appears possible to transform the material further by subjecting it to the process of thermal decomposition. The as obtained material has a form of tubes with a diameter of a couple of micrometers that are composed of carbonized cellulose coated with the polyoxoborate–AuNP nanocomposite. This inorganic shell, which covers the outer surface of the carbon microtubes, serves as a scaffold that makes the structure stable. The obtained material exhibits electrical properties of a semiconductor with the width of the band gap of about 0.6 eV, and forms Schottky contact with a metal electrode. We show that the new material is suitable for preparation of the NCTtype thermistor. We also demonstrate application of the new nanocomposite in electrochemistry for modification of the surface of a working electrode. Experiments carried out with three exemplary redox probes show that the electrochemical performance of the modified electrode depends greatly on the amount of AuNPs in the nanocomposite.

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P45. **Electrochemical Communication between *Enterococcus faecalis* Cells and Electrodes Mediated by Osmium Redox Polymers**

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The use of flexible osmium redox polymers as artificial mediators in bioelectrochemical systems attracts attention due to their flexible polymeric structure, which allows them to form stable immobilized multilayers/hydrogels with both enzymes [1] and microbial cells [2, 3, 4] on electrode surfaces. They provide an efficient electron shuttling and a high local saturation of mediating functionalities. Os polymers are of special interest in studying Gram-positive bacteria or other organisms having thick membranes or cell walls and, therefore, are not suitable for direct electron transfer.
We have found that Gram-positive *Enterococcus faecalis* cells communicate with the electrode directly through membrane-located quinones. However, the existence of a thick peptidoglycan layer in the cell wall does not contribute to the generation of a high current. Moreover, the cell is a very complicated complex system and the mechanism of electron transfer has not been explored completely. In accordance with this problem, the aim of this study was to investigate the ability of Os polymers with different chemical structures and redox potentials to activate various redox active cell components involved in the mechanism of intracellular electron transfer.
In this context *E. faecalis* cells were electrochemically connected to the electrode *via* Os polymers and investigated using cyclic voltammetry, chronoamperometry and chronopotentiometry.
This work was financially supported by the European Commission through Marie Curie “BIOENERGY” (project No. 607793).

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P46. **Influence of nanomaterials on bioelectrocatalytic properties of enzymatic electrodes**

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Comparative studies of bioelectrodes based on different nanomaterials (nanoparticles (NPs), nanotubes (NTs), graphene *etc*), or on the nanomaterial with different dimensions, provide the scientific background for the development of high-performance and stable bioelectronics.

We experimentally proved that the improved bioelectrocatalytic signals, when employing nanoparticles (NPs) larger than the enzyme molecule size, are attributed to the inherent area magnification by employing nanostructures, and the size of the NPs in this size domain does not affect the bioelectrocatalytic properties of the NP–enzyme conjugate [1, 2]. These studies were carried out using two-dimensional (2D) and three-dimensional (3D) biocathodes based on bilirubin oxidase immobilized on gold NPs (AuNPs) with a sub-monolayer coverage and a porous AuNP layer, respectively.

Investigation of the bioelectrocatalytic characteristics of glucose-oxidizing bioanodes based on graphene, poly(3,4-ethylenedioxythiophene), and glucose oxidase, immobilized on the surface of various nanomaterials (AuNPs and multi-walled carbon NTs (CNTs) of different sizes (CNTs of different diameters) was performed. We showed that bioelectrocatalytic signals of nanocomposite based bioanodes depend strongly on the nature of nanomaterial and just slightly affected by its dimension [3].

The work has been supported financially by the Russian Science Foundation (project No.14-14-00530).

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P47. **Pinhole permeation of self-assembled ssDNA monolayer on gold electrodes**

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Self-assembled monolayer (SAM) of ssDNA is widely used as a biochemical interface because of their easy and reproducible preparation. The efficient and reproducible packing of ssDNA monolayer on electrode surface is crucial for convenient chemical or biochemical sensor design. In most cases, the behavior of SAM of ssDNA resembles microelectrodes, identified as defects in ssDNA monolayers. This report seeks to advance fundamental insight into issues that impact the structure and behavior of surface-immobilized ssDNA layer. In this work, the homogeneity and properties of SAMs of ssDNA on gold electrodes have been studied by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry [1]. EIS technique was shown to be a very powerful tool for evaluation of structural properties of monolayer. The average radius of the pinholes and the distance of the neighboring pinhole center have been estimated and discussed [2]. The structure and properties of ssDNA monolayer are studied by varying immobilization conditions, including solution ionic strength and ssDNA concentration and length.

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P48. **Various immobilization methods of photosensitizers capable of singlet oxygen generation on solid surface**

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Advances in surface modification procedures has been motivated by developments in nanotechnology and discoveries of various nanoparticles [1]. In particular, immobilization of photosensitizers able to generate singlet oxygen molecule gained research interest finding its comprehensive applications in various areas such as organic photochemistry [2], medicine [3] and wastewater treatments [4]. Creating an ideal material capable of singlet oxygen generation combine a high efficiency of sunlight absorption and a high photostability. Up to now, several effective procedures have been proposed for photosensitizers immobilization including adsorption, inorganic post-modifications and covalent bonding with the polymer matrix [5]. Recently, electrochemical methods gained our group attention for immobilization of phenothiazine derivatives [6, 7].
We report on phenothiazine layers deposited to GC or ITO electrode by three different electrochemical methods i.e. electropolymerization, electrografting and surface-initiated electropolymerization, with the aim to assess their ability of singlet oxygen generation. The first procedure involve simple electropolymerization of phenothiazine onto ITO electrode, the second modification employs the electrochemical reduction of phenothiazines' diazonium salts on the GC electrode and at the end, the third method is based on the electrochemical polymerization from GC surface previously modified with the molecular layer in electrografting. The formation of each phenothiazine layers were confirmed by cyclic voltammetry and UVVis spectroscopy. The illuminated photoactive layers were capable to create their triplet state and transfer their excessive energy to the ground state oxygen and generate active form of oxygen. The yield of this photoprocess was measured by UVVis spectroscopic procedure in which used 1,3-diphenylisobenzofuran (DPBF) as a specific singlet oxygen trapping agent dissolved in organic solvent was used and the activation of photoactive layers was achieved by diode laser with excitation wavelength 638 nm and the xenone lamp equipped with the interference filter 575 nm.

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P49. **An adhesive conducting electrode material based on commercial mesoporous titanium dioxide as a support for horseradish peroxidase for bioelectrochemical applications**

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Porous materials are finding important applications in the fields of science and technology as adsorbents, supports for catalysis and (bio)sensors. Because of their large surface and uniform pore size distribution in the same dimensions as biomolecules (1), mesoporous materials have been immobilized on electrodes and impregnated with biomolecules to form biosensors. Recently, it has been proven that the electrode modified with porous TiO_2 (pore size 5-10 nm) and an enzyme can show enhanced catalytic performances (2).
An adhesive conducting electrode material containing of graphite, biocompatible ion exchange polymer nafion® and commercial mesoporous TiO_2 impregnated with horseradish peroxidase (HRP) is prepared and characterized by amperometric, UV-Vis and N_2 sorption methods. The factors influencing the performance of the resulting biosensor are studied in detail. The optimal electrode material consists of 45% graphite, 50% impregnated HRP-TiO_2 and 5% nafion®. The optimum conditions for H_2O_2 reduction are an applied potential of -0.3 V and 0.1 mM hydroquinone. Sensitivity and limit of detection in the optimum conditions are 1 A M^{-1} cm^{-2} and 1 μM correspondingly. The N_2 sorption results show that the pore volume of TiO_2 decreases sharply upon adsorption of HRP. The preparation process of the proposed enzyme electrode is straightforward and potentially can be used for preparation of carbon paste electrodes for bioelectrochemical detections.

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P50. **Coupling of biochemical reactions with Quantum Dots for light switchable electrodes**

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Quantum dots are small colloidal semiconductor nanoparticle which have been studied with growing interest during the last decade because of their interesting optical properties. By illuminating the QDs with light of a sufficient wavelength electron-hole-pairs can be generated inside the particles. Thereby electrons switch from the valence to the conduction band, followed by a relaxation in the initial state, resulting in light emission. Here the light emission depends on the diameter of the QDs, which allows a size-tuneable fluorescence and makes QDs very popular as fluorescence label [1]. In addition to the optical application, QDs have been used as building blocks in electrochemical sensors for the introduction of a light sensitive element [2]. By the attachment of QDs to the electrode light-induced charge carriers can be transferred between the electrode and the QDs, resulting in a photocurrent which can be used as analytical tool. Depending on the potential, an anodic or cathodic photocurrent can be detected. Anodic photocurrents are caused by electron transfer reactions from a donor in solution via the QDs to the electrode. On the other hand, electron flow from the electrode via the QDs to an acceptor in solution can occur, thus generating a cathodic photocurrent. An effective photocurrent generation depends on different factors such as the quality of the QDs, the coupling of QDs to the electrode, the reaction rates for oxidation or reduction of substances at the QDs and the recombination of charge carriers inside the nanoparticles [2].

For the construction of QD electrodes, we have attached CdSe/ZnS QDs to gold electrodes via different immobilization strategies. Either the synthesized QDs are directly attached on 1,4-Benzendithiol modified electrodes or the nonpolar ligands of the QDs are firstly replaced by ligands with functional groups to provide functionalities for electrode and/or biomolecule interactions. Subsequently the functionalized QDs were bound via chemisorption to the electrode. Afterwards photoelectrochemical measurements are perfomed, showing stable photocurrents in the anodic and cathodic direction. This provides the basis for the combination of the QD electrodes with biochemical reactions. The functionality of the prepared QD electrodes have been investigated by using small redox molecules such as ferrocyanide and ferrocenecarboxylic acid in solution which results in a concentration dependent increase of the photocurrent. This gives access to the construction of mediator based electron transfer chains. For example sulfite oxidase was coupled with ferricyanide and QD electrodes for photoelectrochemical sulfite detection.

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P51. **Microporous Carbon Derived from Intrinsically Porous Polymer Hosts Platinum Nanoparticle Catalyst**

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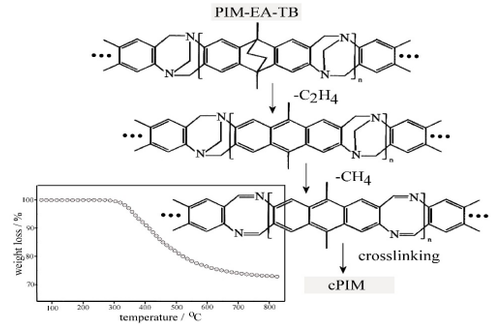
The polymer of intrinsic microporisity PIM-EA-TB has been reported to possess interesting properties for applications in elctrocatalysis[1] and electrochemical membranes[2]. Carbonization of PIM-EA-TB at 500 °C under vacuum for 3 h is shown to produce a novel type of microporous carbon. Figure 1 shows the proposed molecular structure change during carbonization with thermogravimetric analysis data.



Platinum is used widely as a catalyst in fuel cells, solar cells, and in water electrolysis system. The preparation of platinum nanoparticles in combination with different carbon substrates have been reported previously. Here, the microporous carbon derived from PIM-EA-TB provides a simple way to prepare uniform and highly active Pt nanoparticles on a new host. Glucose oxidation and oxygen reduction data are reported.

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P52. **Deposition of charged gold nanoparticles on quartz crystal resonators modified by thiols**

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Immobilization of gold nanoparticles on different electrode surfaces is extensively studied because of their electrocatalytic properties (1,2). Quartz crystal microbalance seems well dedicated tool for these studies (3). Here this tool was applied for determination of the amount of positively (AuNPs+) or negatively (AuNPs-) charged gold nanoparticles deposited on bare quartz crystal resonators and on resonators modified with thiols. The mass of deposited gold nanoparticles was calculated with Sauerbrey equation (4).

First, quartz crystal resonators covered by gold were immersed into solution of given thiol (3-mercaptopropionic acid, 11-mercaptoundecanoic acid or N,N,N trimethyl(11-mercaptoundecyl)ammonium chloride) in ethanol. In the next step modified or unmodified resonators were immersed in water. After stabilization of their resonance frequency signal gold nanoparticles suspension in water was added to stirred solution. Then, the decrease of the signal by tens of hertz was seen.

In order to detect deposited nanoparticles on the quartz crystal resonators surface scanning electron microscopy was used.

This study shows that the largest number of positively charged nanoparticles are adsorbed on bare resonators. On the other hand, the largest number of negatively charged gold nanoparticles are adsorbed on resonator modified by thiols with positively charged functional groups.

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P53. **Wiring of [NiFeSe] hydrogenase via the formation of a dense redox hydrogel network by an electrochemical induced crosslinking process**

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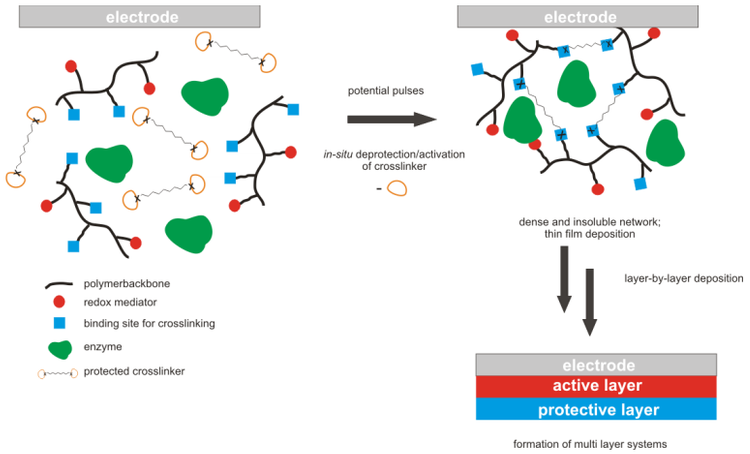
An electrochemically induced and hence non-manual deposition of bioactive thin films onto electrode surfaces from aqueous solutions is of particular interest for the fabrication of enzyme electrodes for amperometric biosensors or biofuel cells. A common strategy for the deposition of such layers is based on the use of pH responsive polymers. Changing the pH in front of the electrode by applying an anodic (generation of H^+) or cathodic (OH^-) potential leads to the precipitation of the polymer. However, such films are only stable within a certain pH range.

The use of bi-functional crosslinkers can circumvent this problem: crosslinking species react with specific binding sites that are attached to the polymer backbone and form an insoluble and stable hydrogel network on the electrode surface. For this, pH-sensitive groups are not required. Moreover, the use of protected crosslinkers exhibiting protecting group which can be electrochemically cleaved allows for a non-manual deposition of such polymer films.



We report on the wiring of a [NiFeSe] hydrogenase via the electrochemical activation of a trityl protected diamino crosslinker and the reaction of this activated species with a polymer backbone that bears epoxy based binding sites and viologen based redox mediators. The viologen moieties were introduced by a “click” reaction between polymer-bound azide moieties and a terminal alkyne species attached to the mediator. The electrodeposited films show a pronounced biocatalytic activity in the presence of the H_2.

P54. **Gold, Palladium nano particles decorated electrochemically reduced graphene oxide nano sheets for voltammetric estimation of Amoxicillin**

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Gold, palladium nanoparticles decorated reduced graphene oxide sheets have been fabricated directly on the surface of glassy carbon electrode, exploiting cyclic voltammetry. The electrodeposited nanosheets have been characterized using FE-SEM, TEM, and EDAX. The electrochemical and electrocatalytic properties of the modification have been investigated by extending its application to the voltammetric estimation of Amoxicillin. The analysis of Amoxicillin has been carried out in the linear concentration range of 30 - 200 µM. High sensitivity and selectivity towards the oxidation of Amoxicillin has been witnessed without any significant interference from biologically important metabolites like uric acid, hypoxanthine, and ascorbic acid. To ensure the practical utility, the sensor has also been successfully invoked in the estimation of amoxicillin in real samples.

P55. **Varying the oxidase/dehydrogenase functions at pyranose 2-oxidase (POx) *via* site-saturation mutagenesis - electrochemical evidences**

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POx catalyzes the oxidation of aldopyranoses at position C2, with D-glucose as preferred substrate, using molecular oxygen, quinones, radicals or chelated metal ions as electron acceptors. The reactivity of POx towards oxygen leads however to several major limitations for its further electrochemical applications due to a high rate of electron discharging and due to limited operational stability of the enzyme film in the presence of enzymatically produced H_2O_2 [1]. Compare to other more common oxidoreductases involved for glucose sensing, POx presents their cumulative advantages [2], by showing higher catalytic rate towards glucose oxidation and using a stable, covalently bound FAD-cofactor. However the oxygen reactivity of POx remains a major limitation for its electrochemical applications. The scope of this study was to eliminate its contribution as a first condition for competitively involving POx in electrochemical applications.

The promising POx candidates from a large library [3,4], generated by site-saturation mutagenesis, were electrochemically screened and characterized in terms of preserved catalytic activity toward glucose and rest oxygen reactivity. Experimental results reveal the existence of several POx-variant, carrying the exchange of one amino acid, with enhanced biocatalytic activity for glucose compare to the wild-type and with an absolute resistance toward oxygen reactivity, however without losing activity with alternative electron acceptor.

Furthermore, the studied mutants of POx were proving to undergo interesting variations of the overall activities towards sugar substrate, oxygen and hydroquinone, thus permitting us to introduce specific roles of the amino-acids played on structural-functional modifications, as it will be presented.

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P56. **DNA biosensors with protective membranes for the detection of DNA interactions in matrices of body fluids**

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Biosensors are highly specific, effective and yet small and cheap analytical devices used for the detection of selected bioanalytes, chemicals, pharmaceuticals and environmental pollutants. DNA based biosensors are analytical devices that integrate DNA as the biological recognition element and a physicochemical transducer. They are successfully used at the detection and investigation of characteristic DNA interactions rather than at the conventional determination of the concentration of an analyte.[1] Electrochemical biosensor is typically represented by an electrode with the surface chemically modified by the biorecognition element. The main problem of analysis with biosensors is the presence of substances in the sample that interfere at the detection of analyte. In such case, the biosensor response may be diminished depending on time of interaction with the sample. These effects can be eliminated by using outer-sphere protective membranes.[2-4]

The aim of this work is preparation and use of an electrochemical DNA biosensor with textured surface for the investigating of chemical DNA interactions with specific chemicals in biological samples of complex matrices such as urine and serum. Results obtained at the search and optimization of polymer protective films on the DNA recognition layer will be presented. Simple polyvinyl alcohol membranes and those doped by halloysite or kaolin have been found as effective barriers able to stabilize the biosensor response in the given matrices. An interaction of acridine yellow as the representative of DNA intercalators has been studied by using cyclic voltammetry with the DNA redox indicator and square wave voltammetry of the guanine and adenine moieties anodic responses.

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P57. **Lipidic cubic phase doped with magnetic nanoparticles as a new drug carrier - voltammetric study of drug release**

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Bicontinuous lipid cubic phases (LCPs) formed by mixing glycerol monooleate with water are non-toxic, bioadhesive and biodegradable in the body. LCPs have a large inner surface and can accommodate the appropriate amount of active molecules of virtually any polarity. Cubic phase is employed to protect the body cells from the harmful effects of the drug and to stabilize the drug when it is unstable. These properties make LCPs highly interesting as the matrix for drug delivery. The addition of magnetic nanoparticles to LCPs opens new possibilities of directing the liquid crystal drug carrier to the desired place using magnetic field. So far, it was demonstrated that in the presence of a moderate magnetic field anisotropic diffusion of hydrophilic drugs in reverse columnar hexagonal phases can be obtained by aligning the domains of the mesophase in a suitable direction using magnetic iron oxide nanoparticles [1]. Another hybrid system with superparamagnetic iron oxide nanoparticles and lyotropic liquid crystal nanoparticles has been shown to provide effective in vivo MRI contrast enhancement in the liver and kidneys or rats [2]. It was also reported that LCP system with hydrophobic magnetic nanoparticles is able to host both hydrophilic and hydrophobic therapeutics in separate compartments, and to release the payload in a space and time controlled manner, upon application of a low frequency alternating magnetic field (LF-AMF) [3]. Previously we have reported that the diamond cubic phase can be a carrier of e.g. anticancer drug – doxorubicin [4]. Now we present application of this drug in the phase in the presence of hydrophilic magnetic nanoparticles (NP_{citric}). The aim of our study was to modify the release rate of drugs from the phase and to target phase particles to a specific location using a magnet. We studied the physical and chemical properties of hybrid material - monoolein/NP_{citric}/H_2O/drug and prepared the cubosomes with magnetic nanoparticles. We investigate the kinetics of release of doxorubicin from MO/NP_{citric}/H_2O system. The structural parameters of hybrid mesophases were characterized by Small Angle X-ray Scattering (SAXS). Release profile of Dox was evaluated using electrochemical methods Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV). These methods are very convenient to monitor the changes of drug concentration directly in the cubic phase.

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P58. **Electrochemical Investigation of the Heme-dependent Aerobic Respiration Process of *Enterococcus faecalis***

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Enterococcus faecalis is a Gram-positive bacterium inhabiting the gastrointestinal tracts of mammals. Furthermore *E. faecalis* is an opportunistic pathogen, which is able to cause nosocomial infections (1). As a facultative anaerobe this species uses a lactic fermentative pathway for energy production and lacks the genes to synthesize heme but can take it up from the surrounding medium. Accordingly when cells are cultivated in the presence of heme and oxygen two heme proteins can be assembled: a cytoplasmic catalase (2) and a membrane bound cytochrome *bd* oxidase (3). As a result a minimal respiratory chain is formed consisting of several NADH dehydrogenases, a demethylmenaquinol and the heme-dependent cytochrome *bd* oxidase (3). Under aerobic conditions the amount of ATP yields up to twice compared to anaerobic conditions (4).
Studies of heme transport mechanisms in other taxonomic groups of Gram-positive bacteria demonstrate that at least two types of functions should be presented in the cell: a cell wall receptor, which couples heme and carries it out through the peptidoglycan layer, and a transporter, which provides penetration through the cell membrane. However, such proteins have not been found in *E. faecalis* yet, and how exactly heme is transported into the cell is unknown.
In this context wild type OG1RF and few mutant strains of *E. faecalis* were investigated using cyclic voltammetry and chronoamperometry under flow injection conditions and under different experimental and culture conditions to find out any possible way of heme transportation.

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P60. **Developing Surface Plasmon Resonance Based Methods for the Study of Living Cells and Colloids**

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The increasing cost of developing new pharmaceuticals and biomaterials has prompted the development of new tools for the characterization of cells and cellular processes. One of the most promising ones is surface plasmon resonance. The technique measures the refractive index at the cell-substrate interface with high sensitivity. The difference in refractive index is also an important contrast mechanism in optical microscopy. However, compared with visualization by microscopy, the considerably higher sensitivity of SPR allows detection of more subtle features (1-4).
Until now the interpretation of SPR data on cells has been based the assumption that the sample can be modeled as a stack of homogenous layers with a certain refractive index. However, such models do not fully accommodate refractive index changes caused by structures such as macromolecular complexes, vesicles, and bulges in the cell membrane that can be regarded as particle-like scatters of light. The effective refractive index of particles dispersed in a media can be calculated by coherent scattering theory (5, 6). We investigated if such theory can be used for interpreting SPR resonance angle shifts for samples of polystyrene latexes. Because it is possible to calculate number concentrations and particle diameters from the coherent scattering theory, SPR has potential to be developed into a powerful particle characterization technique.
The coherent scattering theory was applied to aid interpretation of SPR measurements of cells undergoing exocytosis, which is a process that involves movement of vesicles close to the gold surface, and the uptake of nanoparticles. More exhaustive discussion of these results is given in another presentation from our group.

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P61. **Using upconversion fluorescence nanoparticles (UCNPs) for continuous measurement system for detection of kidney failure**

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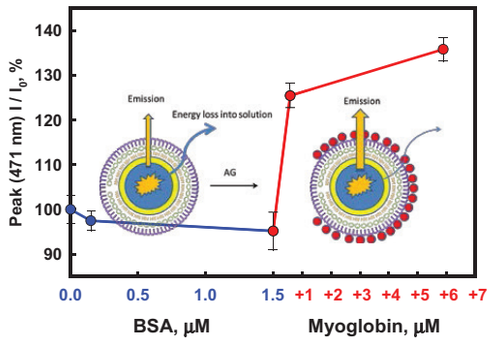
NGAL protein is released from damaged kidney cells and is an excellent biomarker for acute kidney injury following trauma. Upconversion fluorescence nanoparticles (UCNPs), doped with rare earth (RE) ions (e.g., Er^{3+}, Ho^{3+} and Tm^{3+}) which can convert a longer wavelength infrared (IR) radiation (800-1100 nm) to a shorter wavelength fluorescence (400 to 700 nm) via a two-photon or three photon mechanism will be used for NGAL detection proposed in this project. UCNPs are strongly fluorescent, low in toxicity and readily synthesised in water which greatly facilitates further biofunctionalization.

Upconversion fluorescence nanoparticles (UCNPs) made of $NaYF_4$, doped with rare earth ions were successfully synthesised, silicated, aminated, modified with anti-myoglobin antibodies and used for detection of myoglobin as a model analyte, prior to initiating studies on NGAL detection. The anti-myoglobin – myoglobin pair was chosen as a model system for testing of antigen detection on UCNPs since this pair is well characterised within the Millner group [1, 2], we have existing reagents and myoglobin (Mr 17 KDa) is a similar size to NGAL (25 kDa).

The fluorescence spectra of anti-myoglobin and anti-NGAL modified UCNPs show two emission peaks (471 nm and 514 nm) which increase in the presence of antigen. These two peaks were used as the detection signal. The first peak at 471 nm exhibited higher reproducibility and precision than second at 514 nm. Control experiments with BSA and test experiments with myoglobin in the presence of BSA were carried out in order to prove specificity of detection. BSA did not cause any change of emission peak size whilst addition of myoglobin resulted in strong increase of emission peak size. Similar results were obtained with anti-myoglobin adhirons and anti-NGAL antibodies.



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P62. **Label-free electrochemical detection of singlet oxygen-mediated structural changes of BSA**

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Protein oxidation by reactive oxygen species belongs to irreversible posttranslational modifications, which changes protein structure and function and ultimately lead to cell dysfunction and death.[1] Oxidative damages have been studied by different methods, such as fluorescence spectroscopy, HPLC, MS, 2D electrophoresis, EPR, Raman resonance,[1-2] while electrochemical methods were used for this purpose very rarely. We developed label- and reagent-free electrochemical methods for detection of protein damage due to singlet oxygen ($^1O_2$) oxidation. The photosensitized oxidation of bovine serum albumin (BSA) was studied in sodium phosphate buffer using the tris(2,2'-bipyridine)ruthenium(II) $[Ru(bpy)_3]^{2+}$ complex as photosensitizer[3] by square wave voltammetry at glassy carbon electrode and by constant current chronopotentiometry at mercury electrode. $^1O_2$-mediated changes in oxidation Tyr and Trp signal of BSA at carbon electrode were obtained. Chronopotentiometric peak H of BSA at Hg electrode increased during $^1O_2$ treatment, what indicated that irradiated BSA was more susceptible to the electric field-induced denaturation than unirradiated BSA. We obtained similar results with urease, where also enzymatic activity was studied. These results together with previous ones obtained with proteins,[4] such as p53, AGR2[5] showed interesting properties of surface-attached proteins and offer simple and inexpensive tools for protein research important in present proteomics and biomedicine.

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P63. **Molecularly imprinted conducting polymer for selective carnosine sensing with capacitive impedimetry**

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A chemosensor with a molecularly imprinted polymer (MIP) film as the recognition unit, selective to a carnosine biomarker, was molecularly engineered, devised and fabricated. Molecular structure of the pre-polymerization complex of the carnosine template with the carboxy and 18-crown-6 ether derivatives of *bis*(2,2'-bithien-5-yl)methane functional monomers was thermodynamically optimized by the density functional theory (DFT) at the B3LYP/6-31g(d) level. The calculated high negative Gibbs free energy change, ΔG = -227.4 kJ/mol, indicated formation of a very stable complex. The solution of this complex was prepared and used for deposition of the MIP films on a Pt disk electrode or an Au electrode of the quartz crystal resonator by potentiodynamic electropolymerization. Subsequently, the carnosine template was extracted from the MIPs with 0.1 M NaOH, as confirmed by the differential pulse voltammetric (DPV), X-ray photoelectron spectroscopic (XPS), and Raman spectroscopic measurements.
For carnosine sensing, impedimetric capacity (CI) measurements were performed under flow-injection analysis (FIA) conditions resulting in the limit of detection of 20 μM (at *S*/*N*=3). This limit implied suitabilty of the chemosensor for carnosine determination in clinical samples. Due to multiple modes of of carnosine binding to MIP recognizing sites, the CI chemosensor appered be more selective to carnosine than to its common interferences including anserine, carcinine and histidine. Advantageously, the imprinting factor, determined by piezoelectric microgravimetry (PM), was high equaling 14.9.

P64. **Spectroelectrochemistry of poly[*meso-N,N'*-Bis-(salicylidene)-2,3-butanediaminonickel(II)]**

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A new redox conducting poly[*meso-N,N'*-Bis-(salicylidene)-2,3-butanediaminonickel(II)] belonging to the well-known transition metal, Schiff base ligands-based polymers family was synthesized by electrochemical polymerization . The in situ UV-visible, FT-IR-ATR, and low-temperature ex situ ESR spectroelectrochemical experiments unraveled both the charge transfer mechanism of this polymer. With the low-temperature ESR measurements short-living paramagnetic transient species were detected and identified as bisphenolic radical cations. Moreover, structures responsible for the charge transfer in the polymer film and present during polymerization were modeled with the quantum chemistry calculation method using density functional theory (DFT). The resulting polymer film is highly conducting and stable with respect to potential multicycling under cyclic voltammetry conditions. The properties of the polymer were very promising for devising a new electrode material for supercapacitors.

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