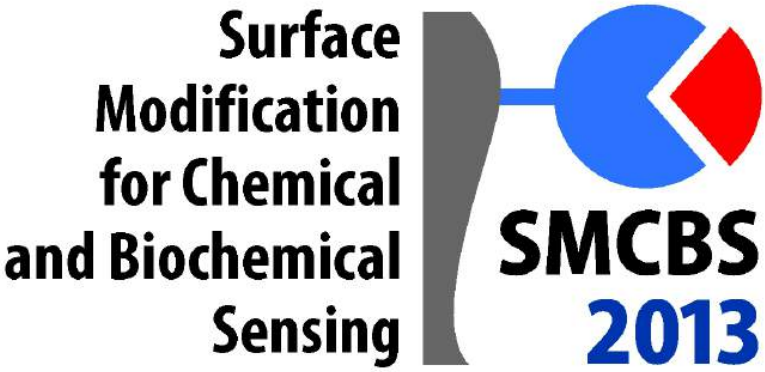



# THE 6th INTERNATIONAL WORKSHOP ON SURFACE MODIFICATION FOR CHEMICAL AND BIOCHEMICAL SENSING

Organized by

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

***Łochów Palace, November 8-12, 2013***

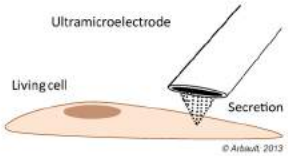
# The Bioelectrochemical Society

BES

The Bioelectrochemical Society (BES) is an international scientific association founded by Giulio Milazzo in 1979 to promote understanding and cooperation among scientists interested in the application of electrochemical concepts and techniques to the fundamental or applied study of living systems.

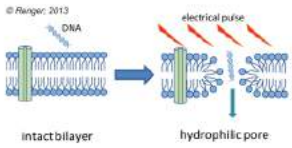
## Content

Bioelectrochemistry includes a broad variety of scientific approaches in using electrochemistry for the analysis of biological systems or in combining biomolecules, cells or subcellular structures with electrodes for different areas of applications such as sensing, drug delivery, bioenergetics a.o.

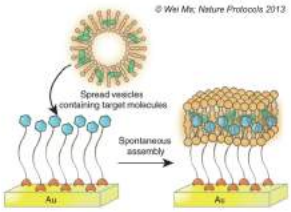



Study of cell behaviour

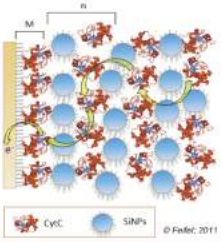
1. Electrified Interfaces and Biosensing
2. Molecular and Cellular Electric Field Effects
3. Biofuel Cells and Signal Transduction
4. Membrane Electrochemistry
5. Electro-medical Case Studies



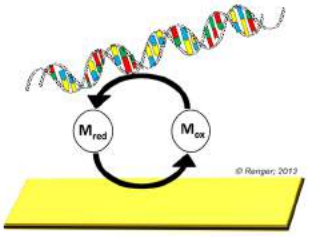

Electroporation of lipid memebranes




Lipid bilayers and protein on electrodes




Multilayer architecture of proteins for analysis




Detection of DNA and DNA damage

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# SMCBS'2013

**THE 6th INTERNATIONAL WORKSHOP**
**ON SURFACE MODIFICATION**
**FOR CHEMICAL AND BIOCHEMICAL SENSING**

# Programme
# &
# Book of Abstracts

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

Łochów Palace
November 8-12, 2013

Interdisciplinary permeation of concepts between chemistry, biology, physics, materials science, microelectronics, and engineering has inspired important new ideas in several research fields including sensing and biosensing. For sensing, surfaces of solid substrates, used for constructing chemical or biochemical sensors, are modified to achieve selective or, in many cases, even specific analyte detection.

The use of sensor-based analytical procedures, originally focused on chemical and biochemical tests, is gaining increasing interest, among others, in environmental toxicity testing, for ecosystem monitoring, clinical diagnostics and therapy, as well as for testing of crops and foods of animal origin.

A continueous increase of interest in sensor-based analytical techniques is manifested by the increase of the number of both scientific papers published and patents registered. Toward this interest, a series of our Workshops is organized. Being encouraged by success of the previous five International Workshops on Surface Modification for Chemical and Biochemical Sensing held in 2003, 2005, 2007, 2009, and 2011 in Poland, the organizers hope that also the coming 6$^{th}$ SMCBS'2013 Workshop will successfully become a platform for researchers to meet for discussing in-depth, exchange and generate ideas. We expect that this activity will stimulate new, and most expectantly, collaborative research. Overview of the interdisciplinary character and the ambience of the SMCBS workshops is well reflected in the comments of one of the SMCBS'2009 Workshop participants.

Apparently, electrochemical aspects of chemical and biochemical sensing dominated former Workshops of this series and many participants were either committed to electroanalytical chemistry or used electroanalytical techniques.

As previous Workshops, the coming one will be focused on the art of both chemical and non-chemical decorating of solid transducer surfaces as well as recognition activity of the resulting sensors toward target analytes. Main topics of the Workshop will cover various aspects of surface chemistry related to chemo- and biosensing in solutions or gases not being limited to:

- Chemical surface reactions
- Self-assembled monolayers (SAMs)
- Langmuir and Langmuir-Blodgett (LB) films
- Preparation and properties of supported membranes
- Chemically modified electrodes
- Enzyme modified electrodes and polymer modified electrodes
- Novel techniques and instrumentation for examining surfaces
- Recognition signal transduction and processing
- Detection techniques and protocols
- Miniaturization of analytical systems and the nanotechnology use

Particularly, young researchers, i.e., graduate students, post-doctoral fellows and research assistants, are welcome to contribute their ideas and enthusiasm to stimulate the field of chemical and biochemical sensing. All presentations, and particularly those of young researchers, will be widely discussed within the audience while constructive input of senior scientists is anticipated.

A half-day sightseeing excursion will bring participants closer together for better personal acquaintance and ad hoc discussions in small groups.

We cordially invite you to participate in the Workshop.

**Włodzimierz Kutner and Marcin Opałło**

# SMBCS’13 Program

**2013-11-08, Friday**

13:00 – 19:00 Transfer to Łochów
19:00 – 20:00 Dinner
**20:00 – 22:00 Poster Immobilisation**

**2009-11-09, Saturday**

08:00 – 9:00 Breakfast

09:00 – 10:30 **Morning Session 1** (chairs: Karolien de Wael and Enrico Marsili)

09:00 – 09:40 **Lo Gorton**
Mediated and Direct Electrochemical Communication between Photosynthetic Cells/Membranes and Electrodes

09:40 – 10:00 **Lars Jeuken**
Biomembrane-modified electrodes to study the versatile electron-transport chain in Shewanella oneidensis MR-1

10:00 – 10:15 **Alexandar Karajic**
Development of electrode architectures for bioelectrochemical applications

10:15 – 10:30 **Celia Silveira**
Probing the regulation mechanism of cytochrome cd1 nitrite reductase - A combined spectroscopic and electrochemical study

10:30 – 11:00 Coffee Break

11:00 – 12:40 **Morning Session 2** (chairs: Lo Gorton and Alexandar Karajic)

11:00 – 11:40 **Nicolas Plummere**
Electron relays in electrochemical biosensors

11:40 – 12:00 **Christopher Leger**
Direct electrochemistry of redox proteins and enzymes for studying their mechanism

12:00 -12:20 **Elizabeth Lojou**
Interface functionalization for efficient biological electron transfer: from enzyme orientation to biofuel cells

12:20 – 12:40 **Karolien de Wael**
Electrochemical Aptasensing – Reaching Maximum Residue Limits and Unraveling Biomolecular Interactions

13:00 – 14:30 Lunch

14:30 – 16:30 **Afternoon Session 1** (chairs: Nicolas Plummere and Paula Lopes)

14:30 – 15:10 **Renata Bilewicz**
Switching between drug storage and release by pH –responsive drug carriers

15:10 – 15:30 **Suna Timur**
Targeted surfaces for cell imaging and sensing

15:30 – 16:10 **Gunther Wittstock**
Coupling and monitoring chemical fluxes of microstructured enzyme layers

16:10 – 16:30 **Andreas Ebner**
Sensing single molecules with the Atomic Force Microscope: New approaches in tip chemistry

16:30 – 17:00 Coffee Break

17:00 – 18:35 **Afternoon Session 2** (chairs: Gunther Wittstock and Deepak Rajawat)

17:00 – 17:40 **Francis D'Souza**
Electron transfer dynamics at the photosynthetic model-semiconductor interface

17:40 – 18:00 **Erwin Reisner**
Photoelectrochemical water oxidation with photosystem II and bio-inspired hybrid materials

18:00 – 18:20 **Peter Schoen**
Imaging of mechanical properties of soft matter at nanoscale resolution

18:20 – 18:35 **Britta Lindholm-Stetson**
Detection of nanoparticles at molecularly imprinted polymer

19:00 – 20:00 Dinner

20:00 – 22:00 Poster Session

**2013-11-10, Sunday**

08:00 – 9:00 Breakfast
09:00 – 10:30 **Morning Session 1** (chairs: Paolo Actis and Veronika Ostatna)
09:00 – 09:40 **Gary Blanchard**
Imaging supported lipid bilayers – factors that influence film fluidity and domain structures and molecularscale order
09:40 – 09:55 **Enrico Marsili**
In vivo characterization of extracellular metabolites in Pseudomonas aeruginosa cultures
09:55 – 10:10 **Marta Sosnowska**
Piezomicrogravimetric and impedimetric oligonucleotide biosensors using conducting polymers of biotinylated bis(2,2'-bithien-5-yl)methane as recognition units
10:10 – 10:30 **Ritu Kataky**
Interactions of nanoparticles with lipid bilayers
10:30 – 11:00 Coffee Break

11.00 - 12.40 **Morning Session 2** (chairs: Gary Blanchard and Alina Vasilescu)
11:00 – 11:40 **Danek Elbaum**
Multifunctional NaYF4: Er3+, Yb3+, Gd3+ and Gd2O3 nanoparticles doped by Er3+ and Yb3+ for use in imaging
and photodynamic cancer therapy.
11:40 – 12:00 **Levi Gheber**
Dynamic display of the Major Histocompatibility Complex class I (MHC-I) on the plasma membrane
12:00 – 12:40 **Karsten Haupt**
In-situ polymerisation of molecularly imprinted polymer nanostructures for chemical sensing with holographic and fiber-optical transducers
12:40 – 13:40 Lunch
14:00 – 21:00 Excursion
21:30 – 23:00 Dinner/Banquet

**2013-11-11, Monday**

08:00 – 9:00 Breakfast

09:00 – 10:30 **Morning Session 1** (chairs: Rabah Boukherroub and Tan-Phat Huynh)

09:00 - 09:40 **Andrzej Lewenstam**
Surface effects in routine application of ion-sensors in biomedical analysis

09:40 - 10:00 **Johan Bobacka**
Adjustment of the standard potential of solid-contact ion-selective electrodes

10:00 – 10:15 **Deepak Rajawat**
Voltammetric determination of lead and cadmium using plant refuses modified carbon paste electrode

10:15 – 10:30 **Paula Lopes**
Electroanalysis of Amyloid Formation of Parkinson's Disease α-Synuclein

10:30 – 11:00 Coffee Break

11:00 – 12:30 **Morning Session 2** (chairs: Andrzej Lewenstam and Grzegorz Milczarek)

11:00 – 11:40 **Sergey Piletsky**
Plastic antibodies

11:40 – 12:00 **Michael Whitcombe**
Integrating molecularly imprinted polymers with sensors and assays

12:00 – 12:20 **Rabah Boukherroub**
Preparation and sensing properties of reduced graphene oxide

13:00 – 14:30 Lunch

14:30 – 16:30 **Afternoon Session 1** (chairs: Sergey Piletsky and Celia Silveira)

14:30 – 15:10 **Sergey Shleev**
Recent advances in biofuel cells

15:10 – 15:30 **Ulla Wollenberger**
Recent progress in bioelectrocatalytic systems with multidomain enzymes

15:30 – 16:10 **Pawel Kulesza**
Development and characterization of biofilm-based hybrid electrocatalytic systems for biofuel cells and analytical sensing

16:10 – 16:25 **Barbara Jachimska**
Bovine Serum Albumin (BSA) Conformation Investigated by Quartz Crystal Microbalance (QCM-D) Measurements, Surface Plasmon Resonance (MP-SPR) and Atomic Force Microscopy (AFM) Measurements on a Silica Surface

16:25 – 17:00 Coffee Break

17:00 – 18:50 **Afternoon Session 2** (chairs: Sergey Shleev and Rui Campos)

17:00 – 17:20 **Mathieu Etienne**
Electrochemical communication between bacteria encapsulated in sol-gel materials and electrodes

17:20 -17:40 **Pawel Krysinski**
Surface modification and miniaturization for implantable electrochemical sensing of catecholamines

17:40 – 18:00 **Paolo Actis**
Single-cell measurements with nanoelectrodes

18:00 – 18:20 **Alina Vasilescu**
EIS investigations on modified interfaces for the detection of allergen proteins

18:20 – 18:35 **Grzegorz Milczarek**
Lignosulfonate-Stabilized Nanoparticles: Proparation and Electrochemistry

18:35 – 18:50 **Veronika Ostatna**
Chronopotentiometric analysis of proteins, polyamino acids and peptides

19:00 - 20:00 Dinner

21:00 – 01:00 Disco

**2013-11-12, Tuesday**

08:00 – 9:00 Breakfast
09.00 - 10.35 **Morning Session 1** (chairs: Wolfgang Schuhmann and Barbara Jachimska)
09:00 – 9:40 **Francesco Baldini**
The optical solution in biosensing
09:40 – 10:00 **Elena Ferapontova**
Design of electrochemical biosensors based on electron transfer properties of DNA
10:00 – 10:20 **Ilaria Palchetti**
Electrochemical biosensing platform for miRNA detection
10:20 – 10:35 **Rui Campos**
Electrochemistry of weakly adsorbed species: Voltammetric analysis of electron transfer between gold electrodes and $Ru(NH3)6^{3+}$ electrostatically interacting with DNA
10:35 – 10:50 Coffee Break

10:50 – 12:00 **Morning Session 2** (chairs: Francesco Baldini and Marta Sosnowska)
10:50 – 11:05 **Tan-Phat Huynh**
Selective determination of explosive nitroaromatic compounds by simultaneous chronoamperometry and piezoelectric microgravimetry using conducting molecularly imprinted polymers (MIPs)
11:05 -11:45 **Wolfgang Schuhmann**
Design of optimized redox polymers. Applications for biofuel cells and photobioelectrochemistry
11:45 – 12:00 Closing
12:00 – 13:00 Lunch

13:00 - Departures

# Welcome

We are pleased and honored to present the program and abstracts of contributions to the 6th International Workshop on Surface Modification for Chemical and Biochemical Sensing, SMCBS'2013, organized by the Institute of Physical Chemistry of the Polish Academy of Science in Warsaw. In the spirit of the previous workshops of this series organized by every two years, we are particularly happy to see so many contributions of young researchers who present their results as short oral communications or posters. Moreover, we are proud to host at the Workshop over a dozen of distinguished scientists who accepted our invitations to deliver tutorial lectures that can stimulate further discussions.

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

As with the previous meetings of the SMCBS workshop series organized in Białowieża (2003), Kazimierz Dolny (2005), Włodowice (2007), Przegorzały (2009), and Lochow (2011), this year's Workshop hosts all the participants in a single location – a Lochow manor house – to give many opportunities to meet for discussions outside the lecture hall and exchange of ideas that may lead to new concepts, collaborations, and joint research projects.

The first two workshops operated within the SURPHARE Centre of Excellence of the European Commission 5th Frame Programme "Competitive and Sustainable Growth", which was established at the Institute of Physical Chemistry of the Polish Academy of Sciences in Warsaw in 2003 till 2005. The present 6th SMCBS'2013 Workshop is a part of the activity within the **N**an**O**technology, **B**iomaterials and A**L**ternative **E**nergy **S**ource for **E**RA Integration (FP7-REGPOT-CT-2011-285949-NOBLESSE) Project of the European Commission organized under auspices of the Bioelectrochemistry Section of the International Society of Electrochemistry and the Bioelectrochemical Society.

The Organizing and Program Committee is particularly grateful to the participants who contributed to the SMCBS'2013 Workshop and sponsors who supported it financially. Moreover, we are thankful to the authors of the contributions, to the session Chairs, and to the members of the International Scientific Advisory Board.

On behalf of the Organizing and Program Committee, we welcome all the participants and wish you an excellent scientific and social SMCBS'2013 Workshop.

*Włodzimierz Kutner and Marcin Opałło, Warsaw, November 2013*

# Organizers

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# Acknowledgements



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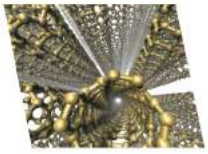

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# Acknowledgements

The European 7th Framework Programme, FP7-REGPOT-CT-2011-285949-NOBLESSE grant is gartefully acknowledged for financial support of the conference organization.

# Single-cell measurements with nanoelectrodes

Paolo Actis,[a] Sergyi Tokar,[a] Jan Clausmeyer,[b] Yasufumi Takahashi,[c] Tomokazu Matsue,[c] Wolfgang Schuhmann,[b] David Klenerman,[d] Yuri Korchev,[a]
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Manipulation and analysis of single cells is the next frontier in understanding processes that control the function and fate of cells. We developed a method to fabricate disk-shaped carbon nanoelectrodes whose radius can be precisely tuned within the range 2-200 nm. We successfully applied the nanoelectrodes for high resolution electrochemical imaging of living cells[1-2]. We present here their application for intracellular measurements both in isolated cells and in tissues.

(1) Takahashi, Y.; Shevchuk, A. I.; Novak, P.; Zhang, Y.; Ebejer, N.; Macpherson, J. V.; Unwin, P. R.; Pollard, A. J.; Roy, D.; Clifford, C. A.; Shiku, H.; Matsue, T.; Klenerman, D.; Korchev, Y. E. *Angewandte Chemie International Edition* **2011**, *50*, 9638.
(2) Takahashi, Y.; Shevchuk, A. I.; Novak, P.; Babakinejad, B.; Macpherson, J.; Unwin, P. R.; Shiku, H.; Gorelik, J.; Klenerman, D.; Korchev, Y. E.; Matsue, T. *Proceedings of the National Academy of Sciences* **2012**.

# Fluorescent and Targeting Architectures for Cell Imaging

Didem Ag[a], Muharrem Seleci[a], Rebecca Bongartz[b], Mustafa Can[c], Seda Yurteri[d], Ioan Cianga[d,e], Frank Stahl[b], Suna Timur[a,*], Thomas Scheper[b], Yusuf Yagci[d,f,*]
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[f]*Center of Excellence for Advanced Materials Research (CEAMR) and Chemistry Department, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Saudi Arabia*

Cancer is a serious and widespread health threat which is investigated about its early diagnosis and therapy by most scientists. Early detection of tumor cells is crucial need for an effective cure of diseases. Targeted molecules in cancer cells have a great potential for cell type specific detection in diagnosis. The use of nanomaterials appears to be the most prominent approach to develop an efficient detection method. These nano-scale particles have large surface area and natural functionalities which allow easy structural modifications for altering their pharmacokinetics, improving their extravasations capacity, prolonging their vascular circulation life-time, providing an enhanced bio-distribution *in vivo*, and cause a continuous and controllable delivering efficiency as drug cargoes.[1,2] Among various nano-structured materials, carbon nanotubes (CNTs) are very promising materials for diagnostic,[3] gene [4] and drug delivery[5] applications due to their unique structural and mechanical properties. Single-walled carbon nanotubes (SWNTs) are unique nanostructures used as cargo systems for variety of diagnostic and therapeutic agents. For taking advantage of these structures in biological processes, they should be visible. Therefore, fluorescence labeling of SWCNTs with various probes is a significant issue.

Herein, we demonstrate a simple approach for cell specific imaging and diagnosis by combining SWCNTs with a copolymer poly(*para*-phenylene) (PPP) containing polystyrene (PSt) and poly(ε-caprolactone) (PCL) side chains (PPP-*g*-PSt-PCL). In this approach PPP-*g*-PSt-PCL is non-covalently attached on carboxyl functional SWCNTs. The obtained fluorescent probe is bound to folic acid (FA) for targeted imaging of folate receptor (FR) positive HeLa cells. *In vitro* studies demonstrate that this conjugate can specifically bind to HeLa cells and indicate great potential for targeting and imaging studies.

(1) Torchilin, V. P. Adv. Drug Delivery Rev., 2006, 58, 1532.
(2) Alivisatos, P. Nat. Biotechnol., 2004, 22, 47.
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# The optical solution in biosensing

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Chemical and biochemical sensing is under the extensive research all over the world and many chemical and biochemical sensors are finding increasing number of applications in industry, environmental monitoring, medicine, biomedicine and chemical analysis. Optics can surely play a fundamental role in all these different areas of applications but health-care is surely the application field which seems to have the best future development perspectives, not only considering 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[1-2]; 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[4-5].
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[6-7].
The fundamental basis of chemical and biochemical optical sensing are summarised and the new trends in biophotonics are described.

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# Bioelectrochemical behaviour of the composite PVP-OS/ Chitosan polymer as Mediator with different types of enzymes at graphite electrode

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A new kind of chitosan which was cross linked to the poly ( 4 - vinyl pyridine) osmium bipyridil polymer ( PVP-Os) to prepare a composite ( PVP- Os / Chitosan) as reported[1, 2]. According to this approach the [PVP-Os- (bpy)2-Cl] polymer is covalently connected to the chitosan to make a redox active composite for enzymes immobilization via Glutaraldehyde (GA) or poly (ethylene glycol) (400) diglycidyl ether (PEGDGE) as cross- linker. The forms of these composite showed porous and hydrophilic properties, which increase mass transport, facile electron transport, lead to a decrease in the formal potential of this polymer, derived from a good communication between polymer, chitosan and enzymes. This composite is found to be a useful platform to host enzymes to make biosensors. The glucose sensing ability has been proved with different enzymes, i.e. Aspergillus Niger glucose oxidase (*Asp.nig*GOX), from Myriococcum thermophilum Cellobiose dehydrogenase (*Mt*CDH), glycosylated Pyranose dehydrogenase (*g*PDH), decomposed deglycosylated pyranose dehydrogenase (*ddg*PDH), and glycosylated enzyme from Aspergillus sp. of glucose dehydrogenase (*Asp*GDH) which is commercially available[3], and recombinant from Glomerella cingulata Glucose dehydrogenase (*rGc*GDH) at 0.1M potassium buffer solution (PBS), pH7, vs. Ag/AgCl (sat.KCl).

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# A molecular imprinted polymer approach to detection of the TATAAA oligonucleotide

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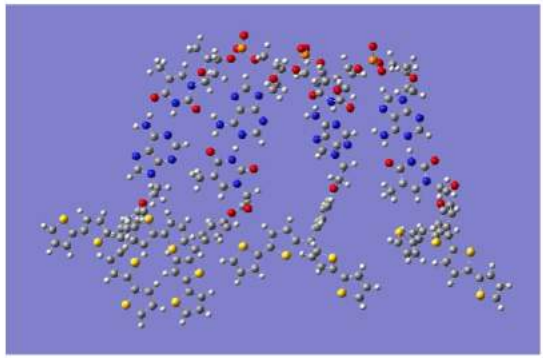
A selective, simple, and rapid procedure of determination of the TATAAA (T – thymine, A – adenine) oligonucleotide was developed. For that, molecularly imprinted polymer (MIP) was prepared. For MIP preparation, 4–{[bis–(2,2'–bithien–5–yl)]methane}phenyl 2–adenine ethyl ether and 4–{[bis–(2,2'–bithien–5–yl)]methane}phenyl thymine acetate were used as electroactive functional monomers. These monomers, with their selective recognition adenine and thymine moieties, were able to form a complex in solution with the TATAAA oligonucleotide target, initially used as a template for imprinting. Electropolymerization of this complex under potentiodynamic conditions in the presence of a selected cross-linking monomer, 4,4'-bisthiophene-3-yl-5,5'-bisthiophene-2-yl-3,3'-(2,2'-bithiophene), resulted in deposition of a thin porous MIP film on a gold electrode of 10MHz quartz resonator of a quartz crystal microbalance (QCM). The TATAAA imprinting was confirmed by X-ray photoelectron spectroscopy (XPS). Next, the TATAAA template was extracted from the MIP film with a strong base solution emptying the imprinted cavities, thus making them sensitive to the TATAAA analyte. These cavities were compatible with respect to their size and shape to those of the TATAAA analyte molecule. With empty cavities, the film was ready for use as a recognition unit of a TATAAA chemical sensor. The detectability of this sensor was investigated under flow injection analysis (FIA) conditions using piezoelectric microgravimetry detection at QCM. The ab initio PM6/3-21G molecular modeling selected the proper geometries of complex of the functional monomers and the TATAAA template.



*A PM6/3-21G optimized structure of the complex of TATAAA oligonucleotide and functional monomers: 4–{[bis–(2,2'–bithien–5–yl)]methane}phenyl 2–adenine ethyl ether, 4–{[bis–(2,2'–bithien–5–yl)]methane}phenyl]*

# Switching between drug storage and release by pH - responsive drug carriers

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Studies of the tumor cells show that the pH of interstitial fluid surrounding the tumor is lower than the pH of normal cells by almost two units [1, 2]. These differences in pH can be exploited for better recognition of the pathologically changed cells and lead us to design new pH-dependent drug carrier systems showing significant decrease in the drug binding strength when pH is decreased from 7.4 to 5.4. Doxorubicin (Dox) selected as the probe drug is currently used to treat a number of cancer types, including ovarian cancer, and multiple myeloma. Incorporation of Dox into appropriate drug carrier reduces the cardiotoxic side effects on the healthy cells and allows the drug to remain longer in the bloodstream, so that more of the drug reaches the cancer cells. [3]

We present two systems where drug storage/release is controlled by the change of pH. Firstly, we show that modification of cyclodextrins (CDs) with a side chain containing aromatic group leads to an increase of the stability of the complex with doxorubicin (Dox). The formation constant evaluated by voltammetry was several orders of magnitude larger compared to that of the unmodified βCD ligand. For the CDs with aromatic moieties connected by linkers containing triazole group, the formation constants of the complexes at pH 5.5 and 7.4 were very different. At lower pH, binding was much weaker due to protonation of the triazole moiety in the linker. The drug was then released from the complex. The toxicity of the synthesized complex and of each of the complex components tested by the MTT assay on two cell lines, the human lung carcinoma and the human cervical cancer cell lines confirmed that the observed pH - dependence can be exploited for drug delivery to the targeted cells.

The other approach was to use the non-toxic, biodegradable lipidic cubic phase (LCP) as a system for immobilizing drugs. Hydrated monoolein forms cubic phase gels with intricate lipid bilayer and aqueous channel architectures. These materials resemble microscopic sponges, and exhibit phase stability, optical transparency and chemical permeability. The cubic phase has a thermodynamically stable structure and due to its amphiphilic nature can be used as a carrier for both hydrophilic and lipophilic drugs. The interactions of doxorubicin with the cubic phase were different at pH 7.4 and 5.4. and lead to much faster kinetics of drug release from the cubic phase at lower pH. A tailored diacidic lipid added to the monoolein cubic phase allows to modify further the release rates of the drug.

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# Polyaniline thin films synthesized via surface-initiated electropolymerization on covalently modified gold surface for sensing application

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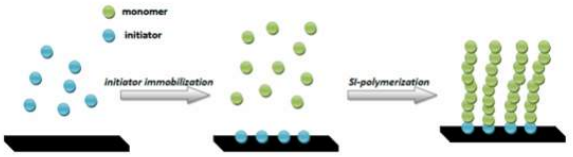
The covalent grafting of polymers to the solid surface is currently of high interest, due to its wide range of application possibilities starting from anticorrosive protection to more complex microelectronic devices. Recently, the most frequent synthesis method is the *surface-initiated polymerization (SIP)*, classified as "grafting from" technique, which consists of two separate steps – the initiator immobilization and the polymer brushes formation. The most important advantage of the route shown below is a high control over the polymer's thickness, architecture and composition.




In the work we present the latest results on the *SI*-electropolymerization yielding the conjugated polymer chains covalently bound to the surface. Here, polyaniline films formation will be demonstrated as the model systems. Two methods of the promoter immobilization have been studied - the Self-Assambled Monolayers formation being the most straightforward, and the electrochemical reduction of diazonium salts being the most universal. The influence of the type of the promoter and its immobilization technique on the properties of the synthesized film will be discussed. The PANi brush-like films were then subjected to the post-modification process, so that *glucose oxidase* molecule is aimed to be covalently bound. The electrochemical and spectroscopic (Raman) results will be presented.

This work was supported by the *National Science Center* (no. UMO-2011/01/N/ST5/03252)).
AB-G is a scholar in the *Project "SWIFT (Stypendia Wspomagające Innowacyjne Forum Technologii)"* POKL.08.02.01-24-005/10 co-financed by the European Union under the European Social Fund

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# Imaging Supported Lipid Bilayers - Factors that Influence Film Fluidity and Domain Structures and Molecular-Scale Order

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Supported lipid bilayer structures have received widespread attention not only because of their potential utility in creating biomimetic devices but also because of their inherent complexity and sensitivity to their environment. Understanding the factors that influence organization and dynamics in such systems could be of immediate relevance to the biological community. Our specific interest lies in the formation of interfaces that could be used to host transmembrane proteins for sensing applications. Knowledge of the relationships between bilayer composition and morphology, as well as the influence of overlayer constituents, is a necessary first step in the creation of useful supported bilayer interfaces. We have constructed model bilayer structures containing phosphocholine, sphingomyelin and cholesterol supported on mica (Figure 1), and have examined the organization of and dynamics within these phase-segregated structures using time-resolved fluorescence lifetime and anisotropy imaging. Our results show that these supported bilayer structures cannot be explained simply in the context of phase segregation of cholesterol and phosphocholine domains, and that the organization of these bilayers depends sensitively on the constituents present in liquid overlayers.

Our image and dynamic data provide a useful starting point for the construction of biomimetic bilayer structures capable of housing biomolecules for sensing applications.

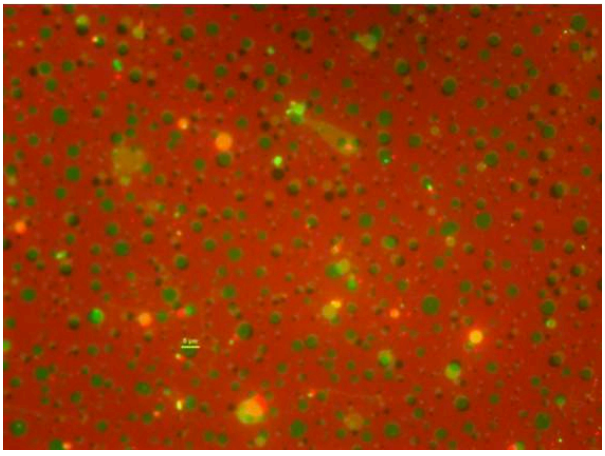

*Figure 1. Fluorescence image of tagged, supported lipid bilayer supported on mica. Red (phospholipid) regions are tagged with a rhodamine chromophore, green (cholesterol) regions are tagged with bo-dipy chromophore.*

# Adjustment of the Standard Potential of Solid-Contact Ion-Selective Electrodes

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Conducting polymers are frequently used as ion-to-electron transducer in solid-contact ion-selective electrodes (SC-ISEs), which has opened a route towards durable potentiometric ion sensors. However, such SC-ISEs often show variations in their standard potential which can be related to the electrochemical properties of the conducting polymer transducer.

One of the unique properties of conducting polymers is that they can exist in various redox states (doping levels). While this property may in fact be the main reason for unwanted variations in potential with time, the same property also offers a unique possibility to electrochemically control the potential of such SC-ISEs where conducting polymers are used as the solid contact. This issue will be discussed for the case where poly(3,4-ethylene dioxythiophene) doped with poly(sodium 4-styrenesulfonate), i.e. PEDOT(PSS), is applied as transducer in potassium ion-selective electrodes.

PEDOT(PSS) was thus electrodeposited on glassy carbon (GC) disk electrodes and coated with a potassium-selective PVC-based membrane. The experimental results show that the standard potential of the studied type of SC-ISEs can be shifted by applying a potential that deviates from the open-circuit potential of the electrode in the chosen electrolyte solution or by applying current pulses in the nA range. The possibility to adjust and control the standard potential of SC-ISEs in a reproducible and predictable manner may be of importance in practical analytical measurements.

# Driving the electrocatalytic properties through carbon-based functional structured surfaces

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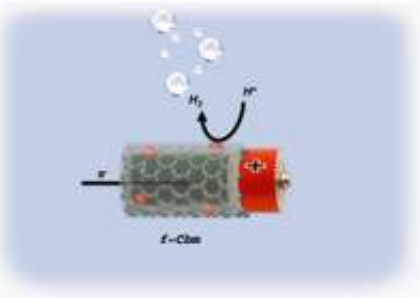
The ability to build hierarchical structures by arranging different building blocks with nanometer-scale precision is one of the most useful aspects of nanotechnology. By combining different materials in the nanometric scale, the physical and chemical properties of the resulting composite may be different to those expected from the simple sum of the individual blocks: this fact can be exploited through the design of appropriate functional materials. In this context, focusing in the field of electrocatalysis, we developed a new carbon-based nanocomposite for the high efficient electrocatalytic hydrogen evolution from water, in mild aqueous conditions. Carbon-based materials have emerged as highly beneficial building blocks for the preparation of various catalysts[1] and, in the last years, hybrids based on MWCNTs and inorganic materials have received great attention for the hydrogen evolution reaction (HER)[2].

In this work we report the study of a nanomaterial based on the synergic combination between titanium dioxide, palladium nanoparticles and functionalized MWCNTs as a cathode for hydrogen production. In our strategy the Pd nanoparticles are the catalytic active sites, titanium dioxide is the scaffold in which the nanoparticles are embedded, and MWCNTs are used as a robust support to increase the conductivity of the system. Here, we have demonstrated that the electrocatalytic properties of the nanomaterial are given by the combination of the three building blocks (strongly enhanced by the presence of the MWCNTs), that are able to generate hydrogen in a very efficient way. Indeed, by means of electrochemical techniques we have quantified the catalytic performances of our system: $TOF_0$ = 242$h^{-1}$, high stability over time and a faradaic efficiency of 90%.



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# Preparation and sensing properties of reduced graphene oxide

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Graphene has attracted a great deal of scientific and technological attention in recent years due to its remarkable electronic, mechanical and thermal properties. Due to its low cost of production, large specific surface area and abundant surface chemistry, graphene has shown great promise in the development of novel composites, biosensors and catalysts (1-2). Graphene has been shown to be an effective biosensing interface of different biomolecules and biologically relevant molecules such as $H_2O_2$, glucose, dopamine, ascorbic acid, uric acid, protein, DNA, cholesterol, histidine, organosulphate pesticides, nicotinamide adenine dinucleotide (NADH), etc (3,4).

Despite the many potential applications that graphene promises to offer, one of the major challenges remains the development of controlled functionalization schemes of graphene. Chemical modification of graphene enhances its solubility, but also allows the electronic properties of the material to be controlled. Both covalent and non-covalent strategies have been used for graphene functionalization (5).

In this presentation, I will focus on the different strategies for the non covalent functionalization of reduced graphene oxide (rGO) and subsequent utilization of the material for sensing of different analytes (6-12).

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# Electrochemistry of weakly adsorbed species: Voltammetric analysis of electron transfer between gold electrodes and Ru(NH3)63+ electrostatically interacting with DNA

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The Laviron formalism, developed for the case of strongly adsorbed species, is widely used for kinetic analysis of surface-confined electron transfer (ET) reactions and determination of ET rate constants $k_s$. However, its applicability and reliability for analysis of ET between electrodes and weakly adsorbed species is unclear. Here is studied the electrochemistry of Rutheniumhexaammine (RuHex) electrostatically interacting with double-stranded (ds) DNA tethered to gold electrodes through an alkanethiol linker. Electrostatic interactions between positively charged RuHex and negatively charged sugar-phosphate backbone of DNA are not strong and depend both on the solution ionic strength and the presence of RuHex in the bulk solution. In this work, electrochemistry of RuHex electrostatically bound to dsDNA strands is studied in the presence of 50 $\mu$M RuHex by cyclic voltammetry and square wave voltammetry (SWV) and the values of $k_s$ were estimated by the Laviron and Komorsky-Lovrić - Lovrić methodologies, respectively. Direct comparative analysis of both procedures evidenced underestimation of the $k_s$ values obtained by the Laviron theory as compared to the Komorsky-Lovrić – Lovrić approach. Underestimation ranged between 40-50% and depended on the DNA surface coverage, being most pronounced at low surface concentrations of DNA, where $k_s$ is maximal. The results evidence better suitability and reliability of SWV measurements in analysis of kinetics of ET reactions of weakly adsorbed species.

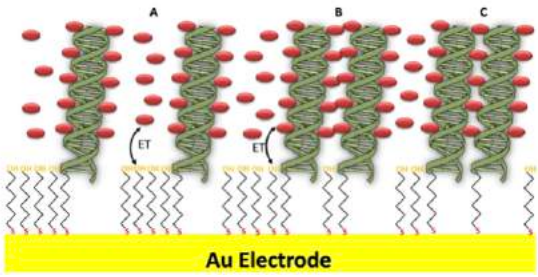


***Figure 1.*** *Schematic representation of the ET reactions between the electrode and RuHex and interactions between RuHex and DNA, varying with the DNA surface coverage $\Gamma_{DNA}$. While at low $\Gamma_{DNA}$ (A) RuHex forms a well-defined wire by binding to the DNA duplex, with increasing $\Gamma_{DNA}$ (B and C) the RuHex molecules may interact with each other and the same molecule of RuHex may even be e.g. shared by two closely standing duplexes. (The tilting of alkanethiols and DNA duplexes versus the surface is not shown).*

# Catalytic hydrogen evolution of reduced and oxidized urease at mercury and amalgam electrodes

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Until recently it was believed that proteins adsorbed on metal surfaces irreversibly denature (1). However using constant current chronopotentiometric stripping (CPS) it was later shown that proteins adsorbed at bare mercury electrodes are denatured when exposed to negative potentials but remain native at potentials close to zero charge (2, 3). Moreover the enzymatic activity of urease adsorbed at mercury and amalgam surfaces was reported (4).

In our work we studied the enzymatic activity and the structure of urease adsorbed at the mercury surfaces (5). We observed that urease adsorbed at the bare solid amalgam surface retained the same enzymatic activity as at the surface modified with dithiothreitol (DTT). After oxidation of urease with diamide the loss of enzymatic activity was detected. Using CPS it was found that urease adsorbed at the bare hanging mercury drop electrode (HMDE) remained in the native state but denatured during the prolonged exposure to negative potentials. The time for which the surface attached protein was exposed to negative potentials was related in CPS to the current density. When current densities were sufficiently high the time of the exposure to negative potentials was very short and the native structure of adsorbed urease was not affected. It was possible to follow surface unfolding of the adsorbed protein in the dependence on the current density or on temperature under appropriate conditions. To avoid the protein denaturation at low current densities, the DTT modified surface was used.

The results suggest that CPS in combination with the DTT modified HMDE as simple structure sensitive method can be used in protein structure analysis.

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# Synthesis and investigation of structural defects in selected derivatives of oligothienylenevinylene potentially applied in organic electronics

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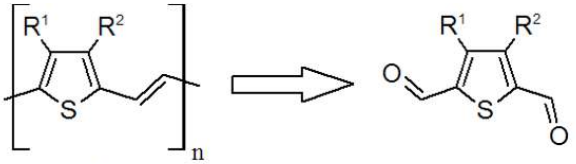
Oligothienylenevinylenes (OTVs) are widely applied in organic electronics mainly in organic field effect transistors (OFET) and organic solar cells (1). In comparison to other classes of conjugated oligomers (especially oligothiophenes) OTV offers the longest effective conjugation length and the lowest values of HOMO-LUMO energy gap (2). Simultaneously it doesn't show any fluorescent emission (3). Although OTV derivatives were first synthesized more than forty years ago (4), methods of their synthesis were poorly described. It should be noted that properties of these materials strongly depend on the method of synthesis and functionalization of oligomeric backbone.

We would like to present the results of our research involving design, total synthesis and spectroscopic characterization of various oligothienylenevinylene derivatives. The most important issues which were taken into consideration were processability and estimation of the number of defects in resulting materials. Reductive coupling (5) of 2,5-dicarbonylthiophenes was chosen as the method of polymerization.




**OTV**

Materials obtained by optimized experimental protocol were characterized spectroscopically applying UV-Vis spectroscopy, infrared spectroscopy and some methods of nuclear magnetic resonance. These techniques supported with mass spectroscopy MALDI afforded us to identify some defects in OTV structure.

Moreover some new OTV derivatives were obtained. Possibility of their application in optoelectronic devices was initially verified using available spectroscopic techniques.

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# Scanning Electrochemical Microscopy Interrogated Immunoplatforms for Sulfonamide Antibiotic Residues in Milk

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Scanning electrochemical microscopy (SECM) is a powerful scanning probe technique that allows a high resolution imaging of electrochemical processes and is also capable to provide quantitative information on the electrochemical properties of a surface.[1] On the other hand, milk and dairy products industries are among the sectors most affected by the presence of antibiotic residues, not only because of the risk of chemical poisoning, allergic reactions, and the development of mechanisms of bacterial resistance, causing a serious threat to human and animal health, but also because of important economic losses derived by the inhibitory effect of these biocides in fermentation processes involved in the production of cheese and other dairy products.[2]

Here the preparation and performance of two SECM approaches for the interrogation of immuno-sensing platforms for sulfonamide antibiotic residues detection in milk is presented. A direct competitive immunoassay was performed involving an antibiotic horseradish peroxidase (HRP)-labeled analog and using selective capture antibodies immobilized on the surface of Protein G-modified glassy carbon plates. Both qualitative and quantitative information for sulfonamide antibiotics residues, employing sulfapyridine as a model compound, was achieved in milk solutions.

Two approaches were investigated for the interrogation of the immunoplatforms with SECM. In a first approach, the sample generator / tip collector mode of SECM was used, involving the reduction of benzoquinone (BQ) generated upon the oxidation of hydroquinone (HQ) at the modified substrate surface through the HRP-catalyzed reaction in the presence of $H_2O_2$ as enzyme substrate. Quantification was accomplished by recording approach curves and plotting the dependence of the measured reduction currents as a function of antibiotic concentration in the different milk solutions.

A second approach involving the enzyme-catalyzed deposition of silver nanoparticles and subsequent interrogation of the modified surfaces in the feedback mode of SECM was developed. In this approximation, $[Fe(CN)_6]^{4-}$ was used as sensing probe and a competition between the tip and the modified glassy carbon plate for the oxidation of ferrocyanide was used in order to achieve a higher resolution in the visualization of the deposited silver-nanoparticle spots.

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# Self-assembled monolayers composed of various phenylboronic acid derivatives

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Chemical sensors are small devices able to collect and transform chemical information into readable (mostly electrical) signals. Because of their small size and low cost per single analysis they are a considerable alternative to classical instrumental methods. In order to assure good working parameters of such a device, a proper receptor layer should be prepared. One of many methods of creating of such a layer is the formation of a self-assembled monolayer of receptor molecules on the surface of planar transducer. In our work we have chosen to use arylboronic acids as a probe molecules.

Arylboronic acids are a group of organic compounds, which are a subject of an interest of many research groups, due to their ability to bind molecules with diol moieties, inorganic anions (like $F^-$) and cations (like $Cu^{2+}$). For this reason, arylboronic acids have been utilized to obtain chemical sensors sensitive to inorganic ions, carbohydrates, catecholamines or even large biological molecules (1,2). Although many spectroscopic systems using those compounds have been developed, only several works are devoted to the design of electrochemical sensors (3).

In this presentation a comparison of different self assembled monolayers consisting of various boronic acids derivatives will be shown. The ability of binding of several analytes such as fructose and fluoride anions will be presented. The influence of different electrode types (policristaline disc electrodes and miniaturized planar electrodes with Au (111)) on properties of formed monolayers will also be described.

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# Electrochemical Aptasensing ? Reaching Maximum Residue Limits and Unraveling Biomolecular Interactions

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A highly competitive and hot topic in developing biosensors is the use of aptamers, also known as 'chemical antibodies', as bio-recognition compound. Aptamers (single strand (ss)DNA or RNA) are synthetic oligonucleic acid sequences which can bind to their targets with high affinity and specificity due to their flexibility. In addition, they are stable and can be employed in extreme conditions. Moreover, these oligonucleic acids can be easily modified by attachment of functional groups without affecting their affinity. Electrochemical sensors with immobilized aptamers as sensing elements are called electrochemical aptasensors. The high selectivity of these sensors is a result of the unique properties of the aptamers.

In this work (1-2), different immobilization strategies will be discussed aiming the development of aptasensing devices for the detection at MRL (maximum residue limit) level of environmentally important molecules such as antibiotics. The biomolecular interactions are investigated in depth. Additionally, the shortening of the selection procedure of aptamers is described by using a computational method.

Pilehvar S.; Dardenne F.; Blust R.; De Wael K. Analytical Chemistry Aptasensing of chloramphenicol in the presence of its analogues: reaching the maximum residue limit.2012, 84, 6753-6758

Pilehvar S.; Ahmad Rather J.; Dardenne F.; Robbens J.; Blust R.; De Wael K. Biosensors and Bioelectronics Carbon nanotubes based electrochemical aptasensing platform for applications in human blood serum, accepted

# Aminoacid Intercalated Montmorillonite Scaffolds for Enzymatic Biosensing Applications

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Clays have been attractive and structures due to their ion-exchange properties, well-defined layered structures, mechanical and thermal stability. With these significant properties, clays generate efficient matrices for immobilizaion of biomolecules and cells used at biosensors, bioremediation or bioreactor processes [1, 2]. The fast and easy immobilization of properties of clays such as montmorillonite (Mont) and laponite have been used for many enzyme biosensors and allow sensitive measurements to be made [3, 4].

Mont Mont has a central octahedral sheet of alumina fused between two external silica tetrahedral sheets and oxygen which is from the octahedral sheet and is also a tetrahedral silica. In its pristine form, the excess negative charge is balanced by hydrated cations (Na+, Li+, Ca2+) which exist in the interlayer [5]. However, pristine clay minerals can suffer from poor selectivity and restricted adsorption capacity. These limitations can be overcome by functionalization of these materials with specific organic groups like amine salts or amino acids. Amino acid intercalated clays (especially layered double or Mont) has been utilized in waste water treatment and tissue engineering but not seemed in biosensing applications.

Herein, we present a novel biosensing platform using amino acid intercalated Monts. Glycine, glutamic acid and lysine were used as modifiers. Glucose oxidase (GOx) was chosen as a model enzyme and immobilized on the glassy carbon electrode *via* clays in the presence of bovine serum albumine and glutaraldehyde. During glucose oxidation by GOx, the amount of oxygen is decreased in the bioactive layer and consumed oxygen affects the electrode signals, it was proportional to substrate concentration and followed at – 0.7 V *vs*. Ag/AgCl. After testing the influence of working pH and matrix composition, GOx based clay biosensors were characterized and applied to detect glucose in some beverages.

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# Electrocatalytic synergy on nanoparticulate films prepared from oppositely charged platinum and gold nanoparticles

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The film gold-platinum nanoparticulate electrodes were prepared by subsequent drop deposition of suspensions of oppositely charged Au and Pt nanoparticles on indium tin oxide surface. These electrodes were characterized by scanning electron microscopy and cyclic voltammetry and were applied for glucose electrooxidation in alkaline solution. These nanoparticulate films exhibit electrocatalytic synergy for the glucose oxidation. The onset potential is significantly lower for films made of Au and Pt nanoparticles as compared with the films made of Au or Pt nanoparticles. The electrocatalytic synergy probably results form close proximity of the surface of gold and platinum nanoparticles attracted by oppositely charged functionalities.

# Electron Transfer Dynamics at the Photosynthetic Model-Semiconductor Interface

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The relation between energy positioning, adsorption geometry, and electron transfer dynamics for donor-acceptor photosynthetic model compounds adsorbed on mesoporous $TiO_2$ surface will be presented. Several Zn-porphyrin (ZnP) and Zn-phthalocyanine (ZnPc) electron donor and fullerene electron acceptor photosynthetic model compounds are designed to build dye-sensitized solar cells (DSSC). It has been found that the solar cell efficiencies normalized for surface coverage ($\eta_{rel}$) are affected by the molecular spacer connecting the porphyrin sensitizer to the $TiO_2$ surface, orientation of the dye molecule, the sensitization conditions (solvent and time) and dye aggregation. Ultrafast transient absorption spectroscopy shows that the forward and reverse electron transfer rates are strongly dependent on the spacer and sensitization conditions. These results also indicate that the electron transfer between sensitizer and $TiO_2$ occurs "through-space" rather than "through-molecular spacer". Implications of these findings for optimized solar energy/fuel production, and future sensor/biosensor development will be discussed.

# CVD graphene: a promising platform for enzyme immobilization in non-invasive glucose sensing

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The development and commercialisation of glucose biosensing has expanded enormously since Clarks and Lyons described the first enzymatic glucose sensor in 1962. However, many challenges remain with respect to rendering these devices non-invasive. The "Glucowatch" from Cygnus Inc., for example, was a minimally invasive, transdermal device based on reverse iontophoresis[1], that did not succeed on the market due to (*inter alia*) low sensitivity, a long warm-up period, skin irritation, cost and calibration issues. Graphene platforms may impact significantly on the biosensing parameters of such transdermal devices through their extreme sensitivity to functionalization, increased speed of detection, ability to be miniaturized and multiplexed, and mechanical flexibility.

We present results on an electrochemical enzymatic glucose biosensor based on chemical vapour deposition (CVD) graphene that has been tested over a range of glucose concentrations, in the presence of oxygen. CVD production generates a low cost, scalable nanomaterial presenting large graphene domains[2]. We demonstrate good reproducibility with cyclic voltammetry and sensitive analysis of glucose in small volumes ('droplets') of buffer. In the prototypical device, glucose oxidase (GOD), a commonly used enzyme for the quantitative detection of glucose in blood, is attached non-covalently to graphene via a pyrene linker ($\pi$-$\pi$ stacking), and confocal and atomic force microscopies were used to successfully visualise the GOD coverage.

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# Layer-by-layer assemblies of polyelectrolyte modified carbon nanotubes and glucose dehydrogenase for amperometric glucose biosenso

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A novel amperometric biosensor for glucose oxidation has been developed. The layer-by-layer technique (LbL) (1) was employed for sequential immobilization of glucose dehydrogenase (GDH) enzyme on poly(diallyldimethylammonium chloride) (PDDA)-modified multiwalled carbon nanotubes (MWCNTs) deposited on glassy carbon electrode. PDDA is a water soluble, quaternary ammonium cationic polyelectrolyte with adhesion and film-forming properties. It was also found that PDDA improved dispersibility of MWCNTs and facilitate formation of functionalized the CNT-based films (2). Moreover MWCNTs stabilized with PDDA are an effective matrix for immobilization biological systems on the electrode surface. The concept of the LbL assembling approach is based on the electrostatic attraction between positively charged surface of carbon nanotubes modified with PDDA and negatively charged molecules of an enzyme (GDH) (3). The main advantage of multilayer biocomposite is the define increase in amount of biocomponents, which leads to a higher sensitivity of biosensor. In our research the optimum number of layers, pH, as well as the effect of the concentration of nicotinamide adenine dinucleotide in bioelectrocatalytic reaction of glucose oxidation in neutral conditions has been examined.

Our biocomposite were characterized using scanning electron microscopy (SEM) and infrared spectroscopy (FTIR). Electrocatalytic properties towards oxidation of glucose were examined by cyclic voltammetry and chronoamperometry. The results are consistent with the view that our approach enables good control of electron distribution and efficient utilization of GDH within the biocomposite film and leads to sizeable enhancement of glucose oxidation throught significant increase of bioelectrocatalytic currents and by shifting the oxidation potential or decreasing the overvoltage. These biosensor exhibited a good linearity ranging (0-2.5 mM), and it was characterized by a high sensitivity (110 μA $cm^{-2}$ $mM^{-1}$), a low Michaelis-Menten constant (8.86 mM) and as well as a low detection limit (130 $\mu$M).

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# Sensing single molecules with the Atomic Force Microscope: New approaches in tip chemistry

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Atomic Force Microscopy (AFM) has developed to an important tool in life sciences. It allows determining the surface roughness of soft biological samples like cells and membranes at near physiological conditions, label-free, and with a lateral resolution in the nanometer range.
In addition, upgrading the usually inert AFM tip by tethering biological molecules to the tip allows gaining more information. Topography and Recognition Imaging[1] (TREC) combines tapping mode imaging with a biosensing AFM tip[2] and allows to simultaneously map the surface topography as well as to localize specific binding partners[3]. A second technique, also based on the use of molecular sensing bio-functionalized AFM tips, is Molecular Recognition Force Spectroscopy[4] (MRFS). There a biosensing tip is repeatedly approached and withdrawn from a surface containing the corresponding binding partner of interest. Within every force distance cycle a ligand-receptor complex can be formed followed by forced ruptering. By varying the pulling velocities the complex energy landscape can be explored giving insights into kinetic and energetic aspects of the interaction[5].
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# Multifunctional NaYF4: Er3+, Yb3+, Gd3+ and Gd2O3 nanoparticles doped by Er3+ and Yb3+ for use in imaging and photodynamic cancer therapy.

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We synthesized Er3+, Yb3+, Gd3+ doped NaYF4 nanoparticles, with up-conversion of infrared light capable to emit in the visible and ultraviolet range to biosensors application. They could be used also for targeted therapy in cancer, through up-conversion to the ultraviolet radiation. Biological systems excited by the near infrared energy exhibit less autofluorescence than if excited by the visible or the ultraviolet light. Visible emission permits to observe physiologically relevant processes within cells, and the emission of the ultraviolet light allows for the selective elimination of cancer cells by generating free radicals.

We were able to synthesize NaYF4 nanoparticles doped with different amounts of rare earth ions, providing an efficient energy up-conversion. After functionalization by PVP or oleic acid, we were able to introduce these particles into HeLa cancer cells, where we examined their localization in the function of incubation time, particles concentration and presence transfection agent Lipofectamine 2000.

In addition, we synthesized Gd2O3 nanoparticles doped by Er3+(1%) Yb3+(18%) ions by the solution combustion method adding Zn to the starting materials. Entering of zinc ions into the Gd2O3 matrix introduces oxygen vacancies, leading to an increase of photoluminescence intensity due to reduction of the site symmetry of rare earth ions. The properties of Gd2O3 make them applicable in contrast-enhanced magnetic resonance imaging (MRI) technique.

Selection of optimal nanoparticles concentration and time of incubation are important in dynamic imagining studies and has critical influence on cellular viability**.**

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# Electrochemical communication between bacteria encapsulated in sol-gel materials and electrodes

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Recently, whole cells have received considerable attention in fabricating biosensors, bioreactors and biofuel cells, due to the efficient communication with their surrounding environment. In this regard, the utilization of a whole cell as host of intracellular enzymes provides a system with high efficiency and stability [1]. Its ability to oxidize different substrates and to transfer electrons either directly [2] or mediated by chemical redox shuttles [3,4], has provided new opportunities for the development of electrochemical cell-based biosensors.

The electrochemical biosensors require the immobilization of whole cells to retain the microorganisms in close proximity to the electrode surface for higher reactivity and stability of the electrochemical communications [5]. Two different strains have been studied here, *Shewanella putrefaciens* CIP 8040 and *Pseudomonas fluorescens* CIP 69.13. They have been immobilized on glassy carbon in a silica-based sol-gel film, this inorganic material mimicking in some respect the polymeric material that provides mechanical stability in natural biofilms.

In addition, electrochemical mediators, either natural or artificial, have been introduced in the films in order to increase the rate of electron transfer from the bacteria to the electrode. These experiments give us the opportunity to discuss the concept of artificial biofilm in which some strategies involved in a natural biofilm can be reinterpreted.

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# (Bio)fuel cells for smart electronic contact lenses

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We present the very first reports on miniature *ex vivo* operating glucose, ascorbate and oxygen sensitive electrodes, which are combined into (bio)fuel cells (BFCs) and investigated in complex buffers and human tears. Specifically, we show that BFCs operating in human tears do produce significant amounts of electrical energy, enough to power modern electronic devices. Several reports exist of contact lens based electronic devices, *e.g.* glucose sensors and electronic displays, and a BFC could be a potential power source for such applications, to realize self-contained, *i.e.* self-powered and wireless, biodevices, *viz.* electronic contact lenses.

We have previously reported on a membrane- and mediator-less sugar/oxygen enzymatic FC fabricated from three-dimensional gold nanoparticle-modified electrodes based on immobilized sugar oxidizing and oxygen reducing enzymes operating in simple buffers and human physiological liquids.[1] *Corynascus thermophilus* cellobiose dehydrogenase (*Ct*CDH) and *Myrothecium verrucaria* bilirubin oxidase (*Mv*BOx) were used as glucose oxidizing and oxygen reducing bioelements, respectively. A similar design was used in the current studies, however, miniaturization of the biomodified electrodes was performed to allow investigations in human tears. As an alternative to the glucose sensitive electrode, an ascorbate sensitive electrode was designed by modifying electrodes with tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ). Miniature electrodes were fabricated using gold microwires (0.1 mm diameter) modified with gold nanoparticles (*ca.* 17 nm in diameter). Detailed investigations of the created nanostructures were done using SEM, AFM, and electrochemistry.

Rigorous electrochemical characterisation of separate microscale glucose, ascorbate and oxygen sensitive electrodes as well as when combined to FCs was performed in complex buffers and human tears. In human basal tears, the following characteristics of glucose/oxygen BFC were obtained: open-circuit voltage of 0.57 V, power density of 0.8 $\mu$W cm$^{-2}$ at 0.50 V cell voltage[2]. After 24 h of continuous operation at 0.51 V biodevices still retained similar power density profile. The ascorbate/oxygen BFC registered an open circuit voltage of 0.54 V, a maximal power density of 3.1 $\mu$W cm$^{-2}$ at 0.25 V and 0.72 $\mu$W cm$^{-2}$ at 0.4 V, with a stable current density output of over 0.55 $\mu$A cm$^{-2}$ at 0.4 V for 6 h of continuous operation.

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M. Falk, V. Andoralov, M. Silow, M. Toscano, S. Shleev. *Analytical chemistry* **2013**,

Submitted manuscript.

# Design of Electrochemical Biosensors Based on Electron Transfer Reactions of DNA Tethered to Electrodes

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DNA genosensing technologies, exploiting differences in electrochemical properties of single stranded (ss) and double stranded (ds) DNA, allow sensitive and specific genetic analysis based on DNA hybridization (1, 2). Discrimination between ssDNA and dsDNA may be performed either by assaying the inherent redox activity of DNA bases or through reactions of DNA with redox indicators, capable of specific interactions with ss or dsDNA (3) (in this case the electron transfer (ET) properties of individual DNA molecules, such as electronic conductivity of a π-stacked DNA duplex are used in biosensor design (2)), or via variations of electrochemical signal from the electrode-tethered redox-labeled DNA (4).

In particular, redox-labeled DNA beacon systems, in which hybridization of the target DNA to the conformationally robust probe DNA tethered to the electrode results in the electrochemically readable conformational DNA nanoswitching, are attractive for the development of electrochemical genosensors (4-6). In contrast to the established and quite predictable genosensor design exploiting intercalating indicators, the outcome of the electronic DNA beacon systems may be unpredictable. Here I discuss complex mechanisms of ET in redox-labeled DNA tethered to electrodes (5, 7-9). Our kinetic studies of ET in DNA bearing different types of redox probes will be discussed in terms ET rates and the ways they may be modulated and used for selective analysis of single nucleotide polymorphism (SNP). Recent results on directional ET through the DNA double strands, demonstrating a sequence-specific dependence on the mode of the redox probe interaction with DNA and SNP-analytical applications will be reported.

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# Incorporating the transport component of Clostridium botulinum C2 toxin into supported lipid membranes

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Pore-forming proteins, such as the transport component of the C2 toxin produced by *Clostridium botulinum* bacteria, are of biomedical interest since the investigation of protein transport into the cell supplies information about transport functions(1). To study pore-forming proteins outside of the complex and diverse system of the cell, artificial lipid membranes provide a suitable model system for a cell membrane(2). Hence, transport processes and surface properties of ion channels can be studied individually. To fully characterize embedded pores, visualizing them e.g. via atomic force microscopy (AFM) or scanning electrochemical microscopy (SECM) is essential. In order to provide a lipid layer setup for a top-down approach via the mentioned scanning probe techniques, a supported lipid membrane (SLM) system was chosen for this study. The system consists of a solid-supported thiol-based lipid membrane(3,4) and was investigated for its ability to incorporate the trypsin-activated transport component C2IIa of *C. botulinum* C2 toxin. This exotoxin consists of two components, the enzymatically active component C2I and the transport component C2II, which can interact with each other after activation of C2II and develop the toxic effect within the cell(5). C2IIa forms heptameric pores, which are cation-selective, voltage-dependent and spontaneously incorporate into lipid bilayers(6). Since the heptameric pores show ion-permeable activity after addition and incorporation into freestanding bilayers, SLMs were tested for their ability to likewise incorporate such toxin pores. After addition of C2IIa to a SLM, where the gold support is additionally acting as an electrode, an increase in current can be detected via cyclic voltammetry. The current increase gives an estimate of the number of incorporated channels. Furthermore, experiments are targeted towards the visualization of the pores within the membrane using AFM and SECM. First results will be presented.

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# Dynamic display of the Major Histocompatibility Complex class I (MHC-I) on the plasma membrane

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The Major Histocompatibility Complex class I (MHC-I) is a membrane protein expressed by virtually all cell types. MHC-I is loaded in the endoplasmic reticulum (ER) with peptides derived from cytosolic proteins and presents them on the plasma membrane to T-cells. This constitutes the primary mechanism by which most nucleated cells report on possible infection by pathogen or damaged tissue.

Many studies have shown that the lateral mobility of membrane proteins, and particularly MHC-I, is hindered, creating a membrane with heterogeneous distribution of its components. Using Near-field Scanning Optical Microscopy (NSOM), we have shown that MHC-I is found in clusters, ~300 – 700 nm in diameter, on the plasma membrane of cells[1]. Since obstructed lateral diffusion alone cannot explain the maintenance of clusters at steady state, we proposed a model that accounts for plasma trafficking, to explain the persistence of the clusters[2].

The model predicts dynamic clusters of MHC-I, created at an instant, by vesicle delivery, and decaying slowly by hindered diffusion over barriers.

We proved the dynamic nature of MHC-I clusters, and characterized their life-time, using GFP-tagged molecules and Total Internal Reflection Fluorescence Microscopy (TIRFM)[3]. Furthermore, since potential barriers to lateral diffusion have been previously suggested as actin filaments (an integral part of the cell cytoskeleton), we have recently shown that the life-time of MHC-I clusters can be modulated by strengthening these barriers (thus elongating the clusters life-time) or weakening them (thus shortening the clusters life-time).

Recent results also show that inhibition of MHC-I trafficking, using Dynasore, a specific inhibitor of Dynamin, cause the (expected) dispersion of MHC-I clusters.

We will discuss possible implications of our findings on the function of the immune system, as well as new insights into the mechanisms by which the immune system displays an exquisite sensitivity for foreign peptides.

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# Oxygen plasma treatment as an efficient tool for fabrication of biocompatible parylene surface

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Alloys based on iron (SS) and titanium (TiAlV) are the most frequently used orthopedic implant materials. The highly corrosive environment in the patient's organism (37°C, saline conditions) induces adverse changes to the metal surface. The release of heavy metals from such surface up to 10 μg/mL/week is reported to be hazardous and even cancerogenic [1].

Polymer parylene C (poly(chloro-para-xylylene), PPX-C) is a suitable candidate to serve as a protective anti-corrosive coating on metal implants due to biocompatibility, good mechanical properties, hydrophobicity and stability in the body ?uids. Furthermore, the deposition of the polymer can be performed by a chemical vapor deposition (CVD) method, which allows the application of the PPX-C ?lms on complex implant shapes and various kinds of materials, i.e., metallic, ceramic and composite. The optimal 8 μm PPX-C coating is dense and smooth therefore, in order to increase, e.g., cell adhesion [2] and to introduce drugs, it is necessary to modify its surface. One of the most efficient techniques which can be applied is oxygen plasma treatment. The plasma parameters may be adjusted for precise controlling of the modification process (p=0.2 mbar, t=0-60min, P=50W).

To characterize the surface topography of native and modi?ed PPX-C samples, atomic force microscopy in contact mode was used. The surface composition was checked using XPS (determined by the integration of narrow scan C1s and O1s maxima). The oxygen insertion and pores formation has an impact on the hydrophilicity of the PPX-C ?lm, thus induced changes of the surface were followed by the contact angle measurements. For evaluation of cell adhesion and bacteria attachment, the MG-63 human osteosarcoma cell line and *S. aureus* were used.

It was concluded that oxygen plasma treatment is an efficient tool for fabrication of biocompatible PPX-C surface. The generation of nanoroughness in the range of 60-200 nm and formation of polar groups ((C=O, C–O, O–C=O, C–O–O and O–C(O)–O) promotes human cells growth and do not promote bacteria attachment and biofilm formation. At the same time, the modification does not weaken the anti-corrosive protective function.

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# Mediated and Direct Electrochemical Communication between Photosynthetic Cells/Membranes and Electrodes

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Previously we have shown that flexible osmium redox polymers can work as efficient mediators between both Gram– as well as Gram+ bacteria and electrodes, clearly showing that the mediator does not need to pass the inner membrane to be able to shuttle the charge between the cells and the electrode [1]. We have now extended our studies to include photosynthetic organisms/membranes. Successful electrochemical communication between isolated photosystem I and II and electrodes have been known for some time [2,3] however, here we report on electrochemical communication between whole viable photosynthetic bacterial cells (*Rhodobacter capsulatus* [4] and *Cyanobacter* sp.*)* as well as with thylakoid membranes from spinach and electrodes through the use of osmium redox polymers.

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# Antibody-Gold Nanoparticle Bioconjugates and Application to Lateral Flow Tests

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Nanoparticles have become a hot topic in biomedical applications due to their small size, specific characteristics and suitability for manipulations at molecular level. Using the gold probes in biodetection systems allows to develop facile, cost-effective and non-toxic processes. Gold nanoparticle probes generally are modified via surface coating chemicals after their synthesis and labeling with biomacromolecules for various applications [1].

Lateral flow tests, also known as Lateral Flow Immunochromatographic Assays, provides multiple sample analysis. Additionally, immunochromatographic tests which based on gold nanoparticles, enable sensitive measurements in sample analysis [2].

In this work we developed a novel antibody-gold nanoparticle conjugate to apply lateral immunochromatographic assay in the detection of antigen. Initially, colloidal gold was synthesized according to Turkevich method [3]. Subsequently, surface modifications of gold colloids were carried out with 11-mercaptoundecanol and 16-mercaptohexadecanoic acid via covalent bonds. Anti-NTproBNP was used as a model antibody to prepare bioconjugates using EDC/NHS chemistry. Afterwards, the characterization of final and pre-conjugates were analyzed by TEM, UV-Visible Spectrophotometry, Agarose Gel Electrophoresis. Data show that all the conjugation steps were carried out successfully. Finally, antibody-gold bioconjugate was then applied to the lateral flow rapid test kites.

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# A novel conducting polymer as an immobilization platform for biochemical sensing

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Biomolecule-based detection technology has become a dynamic area of research because of its remarkable potential for a variety of applications. To improve stability of the biosensors for different requirements, modification of transducer surface for immobilization of bio-molecule is key point. The use of conducting polymers in the design of biosensors is very attractive because of homogeneous and controllable ?lm character, ability of modi?cation of physical and optical properties, stability and biocompatibility, availability of various type of monomers, reproducible and easy production, ef?cient electron transfer ability.[26-28] The synthesis of novel conducting polymers donates the creativity of the fabricated bio-detection systems. For this aim, a new monomer containing amino groups has been used in this study.

Here we present the fabrication of conducting polymer based enzymatic biosensor. The electrode surface was covered with novel monomer namely 4-amino-N-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzamide (HKCN) via electropolymerization. Then pyranose oxidase was stabilized using glutaraldehyde as a cross-linker. After optimization of biosensors, analytical characterization and surface imaging studies were investigated.

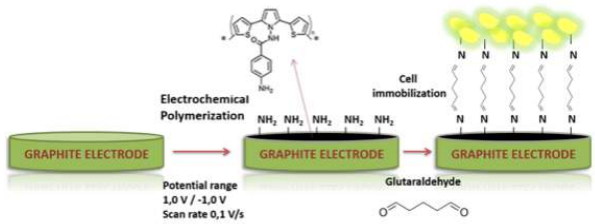


Fig.1 Schematic representation of the proposed biosensor

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# Flow Injection Analysis of Cholesterol Using FFT Admittance Voltammetric Biosensor based on MWCNT-ZnO nanoparticles

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A new electrochemical method was designed for determination of cholesterol by combination of continuous admittance square wave voltammetry method and a highly sensitive biosensor. The new biosensor was constructed using immobilization of cholesterol oxidase (ChOx) on multiwalled carbon nanotubes (MWCNT) and ZnO nanoparticles (ZnO). The biosensor was used in a flow injection analysis system. The special square wave voltammetric method was established based on application of fast Fourier transform (FFT) and continuously calculating the biosensor admittance in a time window. The response of the injected cholesterol samples was calculated by background subtraction and integration of the biosensor signal in the recorded voltammograms in form of coulomb. The method is very sensitive and the response time is less than 8s. The technique was applied as an electrochemical detector in a flow injection analysis system. Detection limit of the cholesterol was 0.05 nM in a linear range from 0.2 to 60.0 nM ($R^2$=0.994).

# Electrochemically Directed Modification of Each Element in Arrays of Homemade Individually Addressable Microelectrodes

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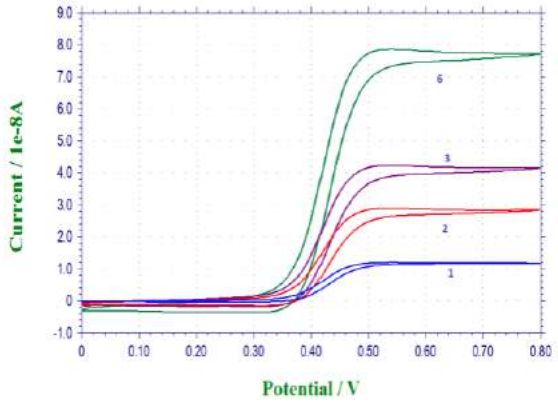
Arrays of microelectrodes maintain advantages of individual microelectrodes (ME); low iR-drop, enhanced diffusion, high signal-to-noise ratio, while enhancing the overall current which avoiding requirement of high amplification of signals and need for efficient electrical shielding of the electrochemical cell [1]. Moreover, when the individual MEs in the array are addressable, they are convenient for fabrication of multiplexed sensors for determination of multianalytes/biomarkers simultaneously or sequentially on a single device.

In this communication, we report electrochemically directed modification of homemade individually addressable MEs in an array with conducting polymers for multiplex biosensor development. Initially, we fabricated cheap individually addressable gold working MEAs from discarded computer chips according to the procedure described by Nascimento *et at* [2]. Electroanalytical behavior of each and combinations of the ME in an array were evaluated by cyclic voltammetric and electrochemical impedance spectroscopic techniques using suitable redox probes (e.g. cyclic voltammograms bellow show the number of electrodes combined and the resulting increase in the limiting current).




Each electrode in the arrays and different combinations produced sigmoidal voltammograms for scan rates even more than 100 mV/s. External interconnection of elements of an array allows amplification of the current by a factor up to n, where n is the number of MEs of the array.

To study controlled, electrochemically guided modification of individual electrodes in a chip, electrochemical polymerization (galvanostatic, potentiostatic or CV technique) of pyrrole and anthranilic acid were performed. Modification of our arrays with these electropolymerizable conducting polymers provided us the following advantages: polymerization was electrochemically directable to each electrode allowing immobilization of more than one biorecognition elements in an array, film thickness can be controlled by controlling time and/or potential of polymerization, polymers are less insulating to the feeble current produced at the individual microelectrode, and the polymer/monomer can be functionalized for covalent immobilization of biorecognition elements (enzymes, antibodies, antigens, oligonucleotides) in biosensors development. This opens an interesting prospect for the development of cheap arrays of electrochemical sensors with multiplexed detection capabilities.

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# Molecular imaging of lipoprotein phenotype by dynamic light scattering. Clinical applications.

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The mechanism of atherosclerosis is not fully elucidated by cholesterol distribution across the density range of lipoproteins. Triglyceride-rich lipoprotein fraction (TRL) is strongly related with the cardiovascular risk level. New data confirmed that non-fasting, postprandial raise in plasma triglyceride is strong predictor of the increased risk of severity and extent of coronary atherosclerosis, myocardial infarction, ischemic heart disease and death in men and women. Techniques suitable for cholesterol-rich lipoprotein characterization are not optimized for TRL detection and analysis. In the field of nanomedicine there is a great demand for technologies that allow the imaging of the size and morphology of triglyceride-rich lipoprotein. Dynamic light scattering (DLS) seems to be the method of choice to assess TRL phenotype, i.e. TRL subclass profile defined by large, light vs. small, dense TRL particle content in TRL pool.

The current study proposes novel approach for understanding how TRL imaging may be related to clinical symptoms of metabolic syndrome and the risk of atherosclerosis. The TRL phenotype analysis using DLS indicates metabolic syndrome severity, as defined by Adult Treatment Panel (ATP) III criteria, and revealed the relation of postprandial variation in triglyceride-rich lipoprotein with the level of atherogenic large VLDL subpopulation. DLS technique is a novel method to allow longitudinal imaging of the lipoprotein subclass pattern. DLS method is sensitive, noninvasive, not influencing lipoprotein nanoparticle size and morphology. DLS results are comparable with data from transmission electron micrographs (TEM) analysis. DLS compared to TEM high-resolution structure analysis tool meets all of the requirements for clinically applicable, simple, not time- and cost -consuming test.

# In-situ polymerisation of molecularly imprinted polymer nanostructures for chemical sensing with holographic and fiber-optical transducers

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We describe a highly selective fiber optic sensor carrying *in-situ* polymerized molecularly imprinted microstructures as the recognition element, which is based on fluorescence for detection by using a fluorescent signaling monomer [1].

Molecularly imprinted polymers (MIPs) are biomimetic synthetic receptors possessing specific cavities designed for a target molecule. Produced by a templating process at the molecular level, MIPs are capable of recognizing and binding target molecules with specificities and affinities comparable to those of natural receptors. These synthetic receptors have considerable advantages over biological recognition elements, as they possess a greater chemical, thermal and mechanical stability. Hence, MIPs have become an interesting alternative to biomolecules as recognition element for biosensing.

The MIP was synthesized by *in-situ* laser-induced photopolymerization in only a few seconds, as a micrometer-sized tip at the extremity of a standard telecom fiber. Photonic and physico-chemical parameters were used to tailor the properties of the polymer micro-objects, leading to well-controlled microstructures. Gold nanoparticles were incorporated into the MIP microtip for plasmonic signal enhancement. To prove our concept, we have first chosen the amino acid derivative Z-L-Phe as a model template for imprinting, and the imprinting effect was monitored with the fluorescent labeled analogue dansyl-L-Phe. The fluorescence was externally collected by optical fibers connected to a spectrofluorimeter, either at the tip level or by collection of the fluorescent signal re-emitted through the arm of a Y-shaped bifurcated fiber. The fluorescent analyte could be detected at low nM concentrations.

In order to be able to monitor non-fluorescent analytes, a naphtalimide-based fluorescent monomer was incorporated into the MIP, which shows fluorescence enhancement when analyte binding occurs. Using this system, a sensor containing a MIP specific for the herbicid 2,4-dichlorophenoxyacetic acid could detect and quantify this analyte at concentrations as low as 0.25 nM. The same system was also applied to several other biologically relevant molecules.

We believe that this study paves the way towards the development of miniaturized portable MIP-based fiber optic sensors, suitable for on-site measurements and real-time monitoring of environmental and biological analytes in complex media.

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# Selective determination of explosive nitroaromatic compounds by simultaneous chronoamperometry and piezoelectric microgravimetry using conducting molecularly imprinted polymers (MIPs)

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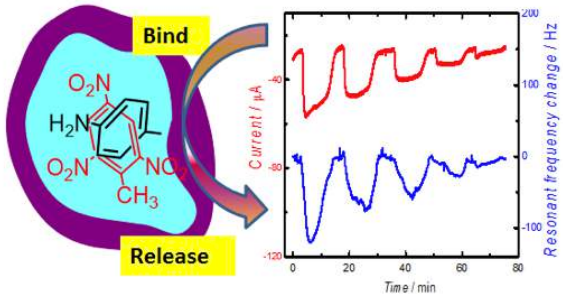


New chemical sensors for selective determination of several explosive nitroaromatic (NT) compounds, including 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), and 2,4-dinitrotoluene (DNT), by virtue of conducting molecularly imprinted polymer (MIP) recognition, were fabricated.[1] Theoretical DFT calculations at the M062X/3-21G* level, as well as experimental shift of the cyclic voltammetry half-peak potential of electro-oxidation of the -$NH_2$ group of bis(2,2'-bithienyl)-(4-aminophenyl)methane **$NH_2$-S2** and fluorescence titrations indicated formation of stable pre-polymerization complexes in solutions. Next, the MIP films were deposited on the Au-coated quartz crystal resonators (Au-QCRs) from solutions of the **$NH_2$-S2** functional monomer and each of different NT templates, at the mole ratio of **$NH_2$-S2**:NT equal to 1:1, by potentiodynamic electropolymerization. Then, the templates were extracted from the MIP films and extraction completeness was confirmed by the disappearance of the XPS signals of the N 1s electron of the -$NO_2$ group. The NT recognition signals of the template-extracted MIP films were transduced to the simultaneous changes of cathodic current and resonant frequency using chronoamperometry (CA) at applied potential of the NT electroreduction and piezoelectric microgravimetry (PM), respectively, under flow-injection analysis conditions. The limit of detection was in the range of hundreds and tens $\mu$M for the CA and PM chemosensor, respectively. Moreover, high selectivity of the sensors revealed was examined by molecular cross-imprinting.

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# Development of inosine-imprinted polymer as a recognition unit in chemosensors for early detection of renal disfunctions

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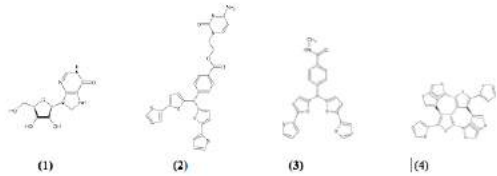


**Scheme 1.** Structural formulas of inosine ***(1)*** bis(bitiophene) derivatized functional monomers ***(2, 3)*** and cross-linker monomer ***(4)*** used for preparation of molecularly imprinted polymer (MIP).

Inosine ***(1)*** is a purine nucleoside composed of hypoxanthine and D-ribose. It is a major degradation product of adenosine with potent immunomodulatory and neuroprotective effects and it has been used to relieve the symptoms of many diseases [1]. It has been also identified as the potential early-warning biomarker of renal disfunction [2]. Due to the vital importance of inosine, many electroanalytical methods have been developed to detect it [3].

In the present work a novel recognition unit for monitoring inosine has been proposed. For that purpose inosine-templated molecularly imprinted polymer (MIP) film has been devised and deposited on signal transducing element. The MIP film was prepared by electrochemical polymerization of bis(bithiophene) derivatives ***(2,3)***, bearing cytosine and amide substituents, in the presence of inosine template and cross-linker ***(4)***. After deposition the template removal was proved with UV-vis spectroscopy and electrochemical techniques. Subsequently, film composition was characterized by infrared (IR) spectrophotometry and X-ray photoelectron spectroscopy (XPS), and its morphology and thickness were studied by scanning electron (SEM) and atomic force (AFM) microscopy. Finally, analytical parameters of the devised chemosensor for inosine detection were evaluated.

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# Bovine Serum Albumin (BSA) Conformation Investigated by Quartz Crystal Microbalance (QCM-D) Measurements, Surface Plasmon Resonance (MP-SPR) and Atomic Force Microscopy (AFM) Measurements on a Silica Surface

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The adsorption of bovine serum albumin (BSA) onto silica from $1x10^{-2}$ M NaCl solutions at various pH values was studied with QCM-D, MP-SPR and AFM measurements. These measurements allowed the determination of both the kinetics of adsorption and the maximum coverage of BSA as a function of pH. The maximum coverage of BSA was obtained for a pH range of 4.5- 5.4, near the isoelectric point of the BSA molecules. At pH >5.4 or <4.5, the adsorbed mass decreased monotonically. AFM images demonstrated changes in the conformation of the BSA. Our measurements enabled us to distinguish among the various conformational states of the BSA molecule; these states were identified by dynamic viscosity studies. In particular, the compact N form prevailed at pH 4-9 and was characterized by an effective length $L_{ef}$ =8.3 nm; the elongated conformations dominated at pH 4.0 with $L_{ef}$ =18.1 nm (E-form) and at pH=3.0 with $L_{ef}$ =26.7 nm (F-form).

Additionally, the adsorbed BSA films were characterized by contact angle measurements under diffusion-controlled transport. This approach demonstrated that the contact angle is sensitive to the amount of protein adsorbed on a silica surface. Comparisons of the QCM-D, MP-SPR and AFM data with other indirect methods (contact angle measurements) broadened the understanding of BSA adsorption patterns as a function of pH. The results obtained in our work confirm the essential role of the highly anisotropic charge distribution of BSA molecules in the adsorption process of this protein.

# Direct electrochemistry and glucose sensing of adsorbed glucose oxidase on 4-(pyrrole-1-yl) benzoic acid functionalized carbon nanotubes

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Our research focuses on the direct electrochemical performance of glucose oxidase (GOx) immobilized on 4-(pyrrole-1-yl) benzoic acid (PyBA) modified multi-walled carbon nanotubes (CNTs). GOx is a homodimer containing two tightly bound flavin adenine dinucleotide (FAD) redox centers embedded deeply in the enzyme (1). Modification of carbon nanostructures allow to obtain thin and organized films, causing a rapid and effective transfer of an electron between the active center of the biocatalyst (GOx) and the surface of the electrode. The presence of PyBA in composite systems significantly improves their stability and introduces new functional groups that have great importance in the enzyme immobilization process of the enzyme on the electrode surface (2).

In this work the stable immobilization and direct electron transfer of glucose oxidase were achieved on the composite film modified glassy carbon electrode. The resulting electrode gave a well-defined redox peaks with a formal potential of about –440 mV (vs. Ag/AgCl) in 0.1 phosphate buffer solution pH=7.0. The electron transfer rate constant was estimated to be 3.15 $s^{-1}$, due to the combined contribution of CNTs/PyBA and GOx. Furthermore, the method for detecting of glucose was proposed based on the decrease of oxygen caused by the enzyme-catalyzed reaction between GOx and glucose. The low calculated apparent Michaelis–Menten constant ($K_M^{app}$) was 10.2 mM, implying the high enzymatic activity and affinity of immobilized enzyme for glucose. It can reasonably be expected that this observation might hold true for other noble carbon nanostructure-electroactive protein systems, providing a promising platform for the development of biosensors and biofuel cells.

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# Potential-supported immobilization of ssDNA on Au electrode surfaces

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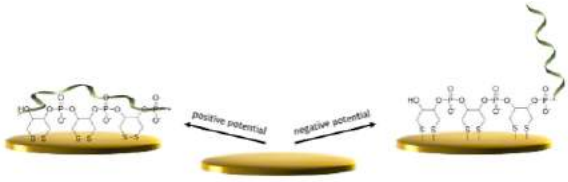
The overall performance of a DNA assay depends to a large extent on the immobilization of ssDNA on the electrode surface [1]. Therefore, the improvement of this step is crucial to achieving better efficiency and reproducibility of DNA sensors.

The main drawback of the mainly used incubation method for ssDNA immobilization is that it usually requires considerable amounts of time - from several hours up to a whole day [2]. Even though the influence of an externally applied potential on the conformation of dsDNA immobilized at the electrode surface has already been shown [3], to the best of our knowledge, the immobilization process itself supported by potential pulse treatment was not yet investigated. This approach is much more efficient compared to the incubation method since it lasts only several minutes and the amount of DNA immobilized at the electrode surface can be controlled by the applied potentials, pulse time(s) and the overall immobilization time.

In this study we used three dithiophosphoramidite units ($DTPA_3$) covalently attached to the DNA probe as anchor sites. During the immobilization process disulfide bonds from each DTPA unit are cleaved and Au-S bonds are formed. Our idea is to support this formation of Au-S bonds by applying potential pulses, i.e. by fast switching between positive and negative potentials (vs. the potential of zero charge, PZC).

Based on the hypothesis that an electrode potential positive of PZC attracts the negatively charged ssDNA strands towards the electrode surface, while an electrode potential negative of PZC causes the repulsion of the DNA strand, it is obvious that the negative potential pulse should not be too long, as the DNA strand could be repelled to the bulk of the solution. On the other hand, if this potential is negative enough, it should support cathodic cleavage of the disulfide bond in the anchor molecule and thus facilitate the formation of the Au-S bond. Therefore, fast switching between carefully selected potentials positive and negative with respect to PZC should lead to a fast and controlled immobilization of ssDNA.

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# Development of oligonucleotide-based electrochemical biosensor for the detection of lead ions

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Among the biologically active compounds utilized as the receptor layers in biosensors, a great interest is given to nucleic acids – double-stranded DNA (dsDNA), single-stranded DNA (ssDNA) and also functional nucleic acids such as DNAzymes and aptamers (1). The most commonly used types of DNA biosensors are: genosensors, in which the hybridization between two complementary DNA strands occurs and the aptasensors, where the aptamer recognition layer adopts the defined conformation as a result of binding to an analyte: simple ions, small organic compounds, peptides, proteins and cells e.g. bacterial (2).
Electrochemical techniques are one of the most popular detection systems applied in DNA biosensors because of their low cost, measurement simplicity and the possibility of miniaturization. Moreover they offer high sensitivity and selectivity as well as independence of sample turbidity (3).
One of the examples of application of DNA biosensors is the detection of metal ions. The nature of interaction between analyte and oligonucleotide sequence is dependant on the given ion: mercury cations exhibit strong affinity towards thymine residues with formation of duplexes: T-$Hg^{2+}$-T (4), while uranyl cations bind to phosphate moieties of DNA sugar-phosphate backbone (5).
The following presentation will be focused on the development of oligonucleotide-based electrochemical biosensor for the detection of lead ions. The receptor layer was formed via immobilization of short thiolated DNA oligonucleotide probes on the surface of gold disk electrodes. The crucial part of sensor preparation was the choice of the nucleotide sequence which will provide the selectivity towards $Pb^{2+}$ ions. The experimental measurements were conducted with utilization of cyclic voltammetry (CV) and square wave voltammetry (SWV) with the use of external redox label – methylene blue and electrochemical impedance spectroscopy (EIS). From the received data it can be concluded that high selectivity towards lead ions is achieved via application of guanine rich oligonucleotide probe (TBA), which was supported by the results of computational chemistry calculations. Moreover the biosensor linear response was in range from 0.05 do 1 $\mu$mol $L^{-1}$ and the limit of detection was of 45.6 nmol $L^{-1}$.

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# Biomembrane-modified electrodes to study the versatile electron-transport chain in Shewanella oneidensis MR-1

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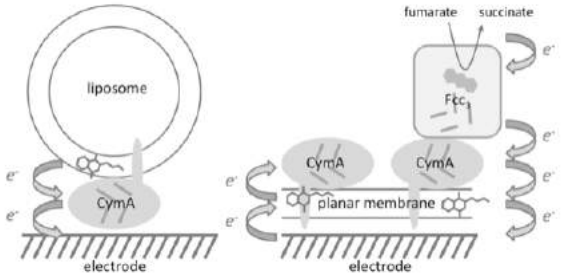


Respiration in *Shewanella oneidensis* MR-1 is unusual in that a single dehydrogenase, CymA, transfers electrons from the menaquinol-7 (MQ-7) pool to a wide variety of terminal reductases. This function places CymA as the central electron distributor of the anaerobic respiratory network. At apparent odds with this function though, protein-film electrochemistry indicates that purified CymA is only able to catalyse MQ-7 reduction, the opposite to the activity required to support its role in respiration. Using solid-supported membranes (SSMs), the catalytic bias of CymA was studied in the presence of one of its redox partners, flavocytochrome $c_3$ ($Fcc_3$) fumarate reductase. CymA was incorporated within SSMs on silicon oxide and subsequent quartz-crystal microbalance with dissipation (QCM-D) data showed that $Fcc_3$ formed long-lived complexes with CymA. The catalytic activity of CymA was monitored by forming SSMs on gold surfaces, where the redox state of MQ-7 in the lipid bilayer is controlled electrochemically. CymA on its own can only reduce MQ-7, but CymA in the CymA-$Fcc_3$ complex efficiently oxidises MQ-7 and passes the electrons to $Fcc_3$ where fumarate is reduced. The turn-over number for MQ-7 oxidation is >40 $s^{-1}$. This is higher than previously reported with non-physiological menaquinol analogues and sufficient to support respiration in *Shewanella*. We conclude that the protein-protein interaction between $Fcc_3$ and CymA regulates the catalytic bias of CymA. This regulatory mechanism might also operate in other members of the widespread NapC/NirT superfamily, of which CymA is a member, and it provides an as yet unexplored mechanism through which bacteria can regulate multi-branched and versatile respiratory networks.

# Sensitive and Selective Electrochemical Detection of Dopamine in Flow System on Carbon Nanoparticulate Electrode

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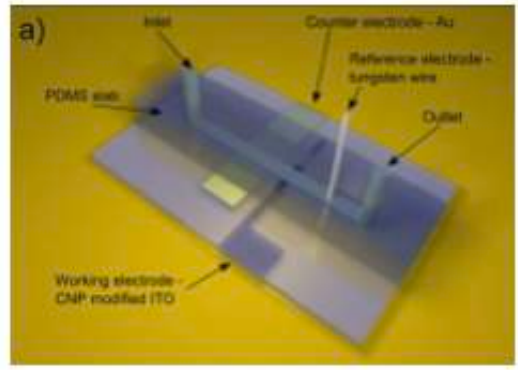
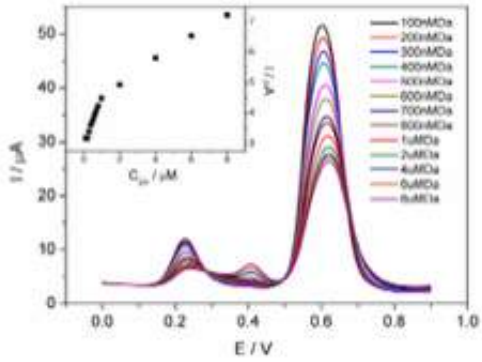
Dopamine (DA), one of the most significant catecholamines, plays a very important role in the functioning of the central nervous system, cardiovascular, renal and hormonal systems as well as in drug addiction and Parkinson's disease [1,2]. The fast and simple determination of low (submicromolar in the cerebral fluid) DA concentrations

becomes more and more important in clinical tests. This is not simple, because its concentration in physiological fluids is very low and there are many interfering substances e.g. ascorbic acid (AA) in high concentration(0.1-0.6 mM) [3].




Here we show that the use electrodes based on hydrophilic functionalized carbon nanoparticles CNPs embedded in functionalized silicate matrix enables selective and sensitive electrochemical detection of DA in flow system, in the presence of interfering substances down to submicromolar level. These electrodes exhibits well defined voltammetry of dopamine (DA) separated from signals corresponding to oxidation of AA and acetaminophen (AC).

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# Nanotubular Oxide Layer on the Ti6Al4V Alloy for Biosensing Applications

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The Ti6Al4V alloy has been for years the most popular titanium implant material due to its mechanical properties, irrespective of the release of vanadium and aluminum, which are still considered as controversial with regard to toxicity. In this work we proposed a novel application of this material. Due to excellent adsorption, hydrophilic and photonic properties, inertness and good biocompatibility, as well as sensing abilities, titania nanotubes have already attracted interest in several applications, ie. as platforms in non-enzymatic glucose sensor, or cancer immunosensor. Thin films of vanadium oxides belong to "smart materials". Coatings made of vanadium oxides are more convenient for practical sensing, electronic, and optoelectronic applications. In this work, we present the fabrication of oxide layers with a highly ordered nanotubular structure with 50nm diameter on both phases of the Ti6Al4V alloy formed by controlled anodization in ethylene glycol with 1% of water and 0.6% $NH_4F$ in 20V for 20 min (Fig.1a). After thermal modification in 600 ?C in nitrogen the nanotubular character is well preserved and vanadium present in oxide layer on both phases. The electrochemical characterization of samples in PBS solution is to evaluate their properties for prospective application in biosensing. The OPC records for nanotube layers on the Ti6Al4V alloy in PBS solution (pH 7.4) (Fig 1b) show stable values for samples annealed in nitrogen (~10 mV vs Ag/AgCl). Cyclic voltammograms recorded for annealed nanotube layers on the Ti6Al4V alloy (Fig.1c) in the PBS solution (pH 7.4) with the scan rate 50 mV/s, are flat. And there are excellent background for electrochemicall detection of catalytic decomposition of p-NPP by bone alkaline phosphatase (BALP, 10ng/ml). This proves that thermally modified oxide nanotubular layer on Ti6Al4V with mixture of titanium and vanadium oxides on both phases may be proper platform for electrochemical detection of alkaline phosphatase for bone turnover monitoring.

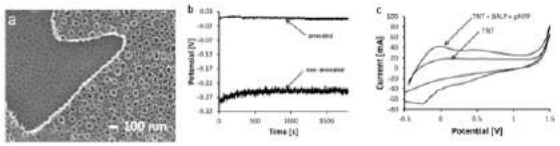


*Figure 1. (a) SEM image of Ti6Al4V surface anodized in ethylene glycol with addition of 1% H2O and 0.6% wt. of NH4F in 20V for 20 min. (b) OCP examination measured for samples annealed in 600 ?C in nitrogen and non-annealed Ti6Al4V nanotubular coating measured in PBS solution for 0,5h. (c) CV recorded for redox reaction of p-NPP in PBS solution catalysed by BALP on Ti6Al4V nanotubular electrode.*

# Electrochemical Ion Extraction under Microfluidic Conditions

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Microfluidic channels are excellent chemical reactors for small scale chemistry and can be used as analytical cells for many purposes. The intention of our work was the application of microfluidic systems to study the electrochemical ion extraction across the liquidlliquid interface between two immiscible solutions generated by the electrochemical reaction of a redox probe dissolved in the organic phase [1]. The scheme in Fig. 1. A presents the fabricated microfluidic chip used in this work. Experiments conducted at static cell were compared to those performed under microfluidic conditions.

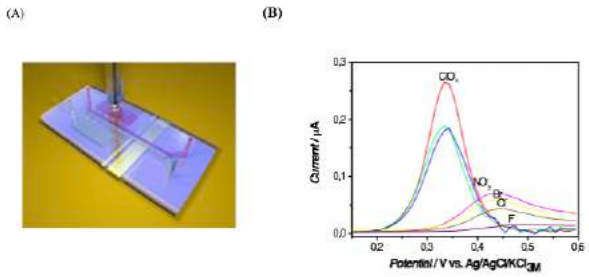


***Fig. 1.*** ***(A)*** *Schematic picture of microfluidic chip used for electrochemical ion extraction.* ***(B)*** *Differential pulse voltammogram of different salts in the aqueous phase recorded under microfluidic conditions when electrochemical ion extraction occurs.*

Preliminary investigations were performed with ferrocene as a redox probe dissolved in an organic N-octyl-2-pyrrolidone droplet deposited on a glassy carbon electrode in contact with aqueous electrolyte. Further experiments were done under microfluidic conditions when transfer energy of anions in aqueous phase and effect of the flow rate on thermodynamics and kinetics of the extraction process were determined [2]. We observed no flow rate dependence on the thermodynamics of the process. The main conclusion is that microfluidic chip can be successfully used as an analytical system to perform electrochemical ion extraction processes.

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# Modification of Electrodes with Interpenetrating Polymer Newtork

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Polymer gels are materials that consist of a three dimensional network filled with solvent. Such materials combine characteristic properties of liquids and solids, i.e. high content of solvent and solid consistency. In addition, some of them can exist in two states: swollen and shrunken depending on the environmental conditions. This phenomenon is called the volume phase transition. The shrinking of the gel is triggered by external stimulus (e.g. temperature and pH) and the volume of the gels during the phase transition could even change by three orders of magnitude. This causes a significant change in the gel properties. The ability of the gels to reverse the changes and their fast response to variations in environmental conditions allowed calling the polymer gels the smart materials.

Interpenetrating polymers network (IPN) are multicomponent materials. In IPN the polymer networks are separated from each other; they are bound only mechanically and there is no chemical bonds between them. This results in maintaining by the composite/IPN the properties of both polymers.

In this paper we present IPN attached to the electrode surface by electrochemically induced free radical polymerization process (EIFRP). Sodium acrylate (SA) and *N*-isopropylacrylamide (NIPA) were used as the monomers. Thin layer of the gels based on SA and NIPA responded to both: pH and temperature. The influence of the change in environmental condition (pH, temperature) on the electrochemical properties of the modified electrodes has been studied.

# Development of electrode architectures for bioelectrochemical applications

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Engineering of electrode surfaces using self-ordering phenomena and growth processes can be steered to create a wide range of structures that allow to adapt structural features to the function of such systems. Herein, we are presenting a strategy for the fabrication of high surface area electrodes for potential applications in miniaturised biofuel cells and biosensors. Gold micro wires serve as a support for generating macroporous gold electrodes with an immobilised enzyme and redox mediator inside the porous structure.

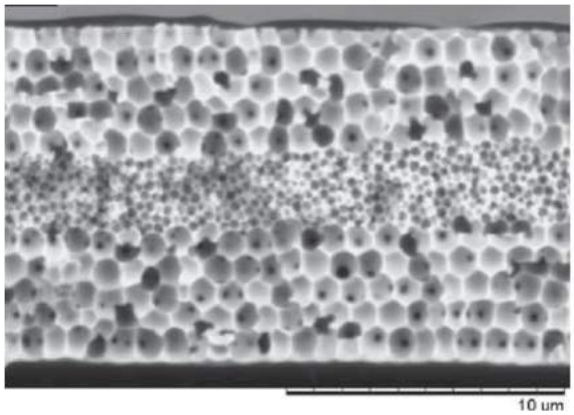


***Figure 1*** *Section of a highly controlled electrode architecture where pores of different size have been generated by a template approach*

We will focus on the improvement of miniaturised coupled systems that have been used for *in vivo* measurement of blood glucose level [1], with a special emphasis on the use of porous electrodes [2,3] with cylindrical geometry. This allows to solve existing problems regarding the low current density and power output of most biofuel cells [4]. The cathodic limitations are addressed through the improvement of the electrical connection between the enzyme and the electrode surface [5] and by increasing the active surface area [6].

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# AA battery - shaped biofuel cell based on carbon nanotubes modified with fructose and sorbitol dehydrogenases

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The biofuel cell is an electrochemical device that converts chemical energy into electrical with the enzymes as catalysts and e.g. glucose or ethanol as fuels [1,2]. These fuels are oxidized in the presence of the appropriate redox enzyme and the electrons are transferred from the anode to the cathode with simultaneous reduction of dioxygen. The glucose and dioxygen are gradually consumed during the work of the biofuel cell. The fall in their concentration decreases the useful power output of such devices. Moreover, in case of many enzymes, the products of the catalyzed reactions are natural inhibitors which also leads to the decrease of the power of the biofuel cell. The constant supply of fuel to the electrodes is also very important. It is crucial e.g. in case of using biofuel cells for powering small medical implants where the powering unit should work in the flow regime.

Most of the studies performed so far focused on one-electron catalytic oxidation of glucose while the maximum number of electrons which could be obtained in this process is twelve. Searching for enzymes that would allow to increase the extent of glucose oxidation is therefore, an important direction of studies aimed at improving of the parameters of biofuel cells.

Recently we have shown recently we have shown the application of carbon nanotubes modified with arylated and perfluorinated groups in order to improve the efficiency of the biocathode in the catalytic reduction of oxygen [3-5]. In the present report, we show our new design of biofuel cell – the AA battery-shaped cell which enables the continuous exchange of substrates. It involves application of nanostructured carbon paper electrodes modified with fructose dehydrogenase and sorbitol dehydrogenase on the anode side, and laccase on the cathode side.

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# Interaction of bioactive molecules and nanoparticles at liquid-liquid interfaces

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Soft interfaces such as the Interface between two immiscible electrolyte solutions (ITIES) or a lipid and an electrolyte solution can provide a mimic for biological systems. Our group has investigated interactions of bioactive molecules and nanoparticles at Interface between two immiscible electrolyte solutions (ITIES) and lipid solution interfaces. . This talk will focus on two diverse aspects of interactions at a liquid-liquid interface.

Tethered bilayers lipid membranes (tBLMs) are commonly used as model membranes. However in biophysical studies free-standing membranes or 'black' lipid membranes are more realistic models of cellular processes. The rates of electron transfer and the electron tunnelling constants in both types of bilayer lipid membranes modified with membrane associated redox molecules and studied using electrochemistry in tandem with impedance spectroscopy will be discussed. Additionally the penetration of gold nanoparticle of different BLMs shows interesting dependence on charge and size. Our results will be presented

2. The investigation of interactions of drugs with proteins is another area of fundamental importance in drug discovery and toxicity studies. A micro liquid-liquid interface can be used very effectively for quantifying drug-protein interactions. Applications to chiral discrimination of drug-protein interactions using ion-amperometry will be presented as a simple and novel method for characterizing the bio availability of drugs.

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# Electrochemical microfluidic system

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Electrochemical real-time detection of biomolecules under non-equilibrium conditions represents a challenge in diagnostic systems. Electrochemical sensors which are integrated into a microfluidic device are in many cases fixed to the surface of the reactor.[1] Understanding of oxidation and reduction processes of biomarkers on the surface of a sensor under irreversible flow conditions plays an important role in the comprehension of molecule-molecule/protein reactions in biological systems. Therefore cyclic voltammetric experiments under different flow conditions (0 to 200 $\mu$L/min) in a microfluidic electrochemical reactor have been done (Fig. 1). To test the setup within the reactor we used the electrochemical well-known redox system $K_3[Fe(CN)_6]$ (50 mM in 0,1 M KCl).[2] The results show that the graphs become flatter with increasing flow rate. This corresponds to the known effect of a varying scan rates (Fig.2). To improve the electrode surface for applying it as a biosensor, nanoparticles were coupled to the gold surface of the working electrode. Experiments also show an effect of the flow rate on modified electrodes.

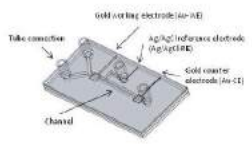


Figure 1: show a prototype of a new microfluidic reactor for upcoming measurements.

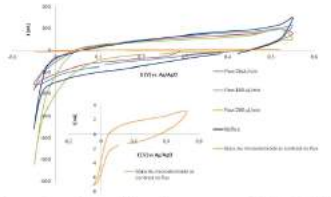

Figure 2: show cylclic voltammograms of $[Fe(CN)_6]^{3-}$ (5 mM in 0.1 M KCl). Dark blue line represents an experiment without flux. Graphs shows the experiment under flow conditions with 20 µL/min (blue), 100 µL/min (red) and 200 µL/min (green) respectively. Orange represents a control measure with an Au micro disc electrode (50 µm Ø) without flow. Scan rate 50 mV/s.

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# Controlled Functionalisation of Electrode Surfaces - an Organic Chemist's Perspective

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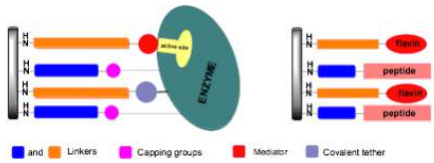
The deliberate modification of electrode surfaces is fundamental to the development of new, more efficient electrochemical devices (eg for sensing, catalysis and energy conversion) and was first investigated almost forty years ago in pioneering work by the groups of Hubbard[1] and Murray.[2] In the intervening period many groups have contributed to the development of a wide variety of approaches for the modification, in order to achieve control over the properties of the electrode surface and to be able to tailor these to a specific application.[3] However many of the subtleties of the effects of the immobilisation method and surface molecular structure remain to be explored.




We are interested in developing methods using organic synthesis[4] that allow both rapid access to a range of modified electrodes and that allow us to control, for example: the partial coverage of electrode surfaces with mixed mono-layers;[5] the incorporation of specific functionality for attachment of biomolecules; and the influence of the bulk mono-layer on the properties of the attached biomolecules. Here we describe progress to date in which we have: used high-through-put chemistry to prepare a library of simultaneously addressable electrodes for NADH oxidation;[6] have controlled the use of linker elements to optimize the attachment of cytochrome C to electrode surfaces; and have shown how partial coverage of electrode surfaces with mixtures of a flavin and other functional groups can be used to alter the redox properties of the flavin.

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# Improving Efficiency of Electrodes in Flow Enzymatic Biobattery and Biofuel Cell

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The main of goal of our study is the construction of efficient bioelectrodes for enzymatic biofuel cell or biobattery. Recently, we demonstrated the utility of arylated carbon nanotubes which expand electrodes practical surface and enhance efficiency of electron shuttling between the enzyme active site and the electrode surface (1-3). Biphenylated carbon nanotubes layer covered with layers of laccase and Nafion modified the glassy carbon surface of the cathode. Bioanode film consisted of a mixture of single walled carbon nanotubes modified with glucose oxidase/catalase and carbon nanotubes modified with ferrocene as the mediator. Three electrode system was applied in the biobattery and biofuel cell in order to follow the behavior of each of the electrodes under fuel cell working conditions in the stationary and flow system. The anode efficiency determines the power output of the whole biofuel cell. Therefore, a semiconductor film was introduced between the carbon nanotubes layer and the electrode surface. The film consisting of either ruthenium oxide and SWCNTs or the conducting polymer containing viologen were investigated as the interlayers responsible for electrical contact between the anode and the active site of the enzyme. Cell parameters e.g. open circuit potential, maximum power density and stability of the system in time were determined.

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# Preparation and frictional investigation of the two-components silanes deposited on alumina surface

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The miniaturization of almost all types of devices and systems is a common practice in an industry field (e.g., electronics, engineering, automotive industry) as well as opportunity of a commercial profit and technological advances. The real effect of a miniaturization in industry are micro-/ nanoelectromechanical systems' (MEMS/NEMS). The use of MEMS technology allows many types of devices to be reduced in size by orders of magnitude (e.g. inertial sensors, optical switch arrays, biochemical analysis systems). Friction and adhesion are crucial aspects that control the efficiency and the durability of MEMS. For the purpose of better mechanical and chemical properties, MEMS surfaces are modified and protected by lubricants. One group of the lubricants which is used in MEMS are organosilane compounds.

Monomolecular films' formation based on organosilanes is one of the strategies that is used for minimizing stiction, adhesion and friction. One of the methods that is used in solving problems which are caused by both the development of a modern technology and the appearance of a miniaturized microelectromechanical systems, is the use of a vapor phase deposition method and multiple patterned chemical functionalities (two-component films). With regard to above reasons, this studies undertakes the theme that aims at producing two-component organosilane films on the alumina surface which are very promising for micro- and nanofabrication technologies future.

Pattern/two-component modification is achieved via gas-phase deposition of the silanes using polydimethylsiloxane stamp. The frictional behaviors of the two-component films of the silane molecules with different chain length covalently absorbed on alumina surfaces, were characterized by the ball-disk (microtribometer) tester. The surfaces of the substrate modified by two-component molecular films were examined by atomic force microscopy (AFM). The measured tribological results showed that the mixing of the fluoroalkylsilane and alkylsilane enhance the lubrication and decrease the friction compared to the one-component thin films.

Presented work will allow to define an influence of the received films' structure on the frictional properties of alkylsilane film/surface systems. Obtained results will enable indicate alkylsilanes that provide the best frictional properties of produced two-component films, which in the future may be used as lubricants for micro-/ nanoelectromechanical systems.

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# Surface modification and miniaturization for implantable electrochemical sensing of catecholamines

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Since the early 70's, electrochemistry has been used as a powerful analytical tool to monitor the electroactive species in living organisms. Since then, and early works of R.N. Adams, who introduced electrochemistry into the area of neuroscience, numerous electrochemical techniques and electrode materials has been used to identify and resolve catecholamines. Particularly, after extremely fast evolution of new surface modifications as well as micro- and nanotechnologies, electrochemistry has been established as invaluable technique, ranging from the experiments *in vivo* to the measurements of exocytosis during the communication between cells under *in vitro* conditions. This presentation highlights recent advances in the development of electrochemical sensors for the selective sensing of one of the most important neurotransmitters – dopamine. Dopamine is an electroactive catecholamine neurotransmitter, abundant in mammalian central nervous system, affecting both cognitive and behavioral functions of living organism. Application of typical electrochemical sensors and biosensors for real time *in vivo/in vitro* monitoring of clinically-relevant physiological analytes, such as neurotransmitters, except several examples, has been restricted to the laboratory use. This is primarily because they suffer from poor selectivity and sensitivity (fouling) when used in biological or biomimicking environment. However, these disadvantages can be overcome by proper surface modifications and miniaturization (down to the range of few μm) of such sensors. The advantages of surface-modified, miniaturized electrodes (whether implantable or not) for electrochemical sensing of redox neurotransmitters, will be briefly summarized during this presentation. We will not attempt to cover large time-span nor to be comprehensive in presenting the enormous literature devoted to electrochemical sensing of neurotransmitters. Instead, we will focus on the last few years, describing the current progress, mostly for the case of wake, mobile animals.

# Development and Characterization of Biofilm-Based Hybrid Electrocatalytic Systems for Biofuel Cells and Analytical Sensing

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We exploited unique properties of biofilms, i.e. polymeric aggregates of microorganisms, in which cells adhere to each other on the electrode surfaces, and they are characterized by of extracellular electron transfers involving c-type cytochromes (heme-containing proteins). Although aqueous suspensions of gold, silver and certain transition metal oxide ($TiO_2$ and $ZrO_2$) nanoparticles tended to inhibit formation of biofilms produced by *Pseudomonas aeruginosa, Staphylococcus aureus and Yersinia enterocolitic* bacteria, application of composite matrices of inorganic nanostructures within porous conducting polymer layers, e.g. of poly(3,4-ethylenodioxythiophene (PEDOT), facilitated growth of robust and mature bacterial biofilms on glassy carbon electrodes. Independent diagnostic electroanalytical experiments showed that biofilms grown by the following bacteria, *P. aeruginosa ATCC 9027, Y. enterocolitica Ye9, Y. enterocolitica AR4, L. monocytogenes 10403S* and *L. monocytogenes 1115*, on inert carbon substrates exhibited by themselves electrocatalytic properties towards oxygen and hydrogen peroxide reductions in neutral media. The processes were found to be further enhanced by introduction of multi-walled carbon nanotubes (MCNTs) that had been modified with ultra-thin layers of organic (e.g. 4-(pyrrole-l-yl) benzoic acid. We expect here attractive electrostatic interactions between carboxyl-group containing anionic adsorbates and positively charged domains of the biofilm with cytochrome enzymatic sites. Co-existence of the above components leads to synergistic effect that was evident from positive shift of the oxygen reduction voltammetric potentials and significant increase of voltammetric currents. The film exhibited high activity towards reduction of hydrogen peroxide. Most likely, the reduction of oxygen was initiated at cobalt porphyrin redox centers, and the undesirable hydrogen peroxide intermediate was further at the biofilm's cytochrome sites. Comparative measurements were also performed using metal nanoparticles (e.g. Au-Pt), conventional enzymes (e.g. laccase), molecular systems (e.g. metalloporphyrins) in the presence and absence of selected bacterial biofilms.

Development of the biofilm and enzyme based anodes was considered too. To facilitate electron transfers between the electrode surface and the redox protein centers, the concept of co-deposition of MCNTs within the bioelectrocatalytic film was also pursued here. First, MCNTs were modified with ultra-thin layers of tetrathiafulvalene (TTF) or poly(dimethyldiallylammonium chloride) (PDDA). The presence of TTF or PDDA was expected to mediate effectively flow of electrons from enzyme active sites through biofilm to the electrode surface. Combination of derivatized MWCNTs with biofilm matrtices and appropriate enzymes produced biocatalytic systems capable of effective oxidation of glucose or ethanol in neutral buffer solution.

# Investigation of the Kinetics of Enzymatic Reactions in under Hydrodynamic conditions

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Protein film voltammetry of redox enzymes has long been used for studies of the mechanistic of enzyme reactions. Hydrodynamic methods offer more information about kinetic and mechanism than experiments held in static conditions. Measurements under static conditions run the risk of confounding kinetic effects with the effects of uncontrolled natural convection [1]. The increase of forced convection usually cause an increase of the current and sensitivity. To eliminate the effect of mass transfer limitations these measurements are generally done using rotating disk electrodes. [2,3]

Here we study the kinetics of a redox enzyme in solution, as well as immobilised on the electrode, using rotating disk voltammetry and voltammetry in a microfluidic system. Controlling the hydrodynamics of the system is possible by both of these setups. The microfluidic setup offers the advantage of a stationary electrode, and can be used to very low flow rates in comparison with the relatively high flow of rotating electrode systems. We will compare the results of measurements using RDE and microfluidics of oxygen reduction by the enzyme bilirubin oxidase at a carbon nanoparticles modified electrode. The measured dependence of the oxygen reduction current on rotation rate, or flow rate, is highly anomalous, with a decrease of the current with increasing flow rate.

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# Introduction to direct electrochemistry for probing molecular aspects of biological catalysis

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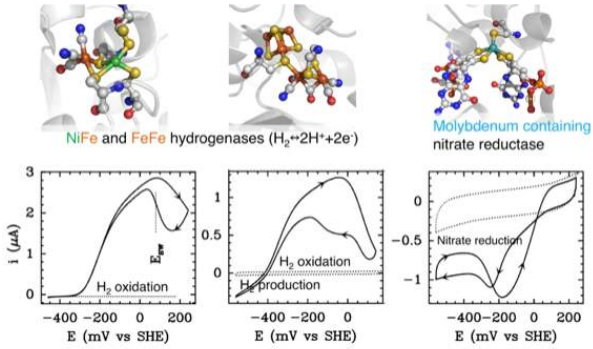
Over the last 15 years, electrochemistry has proved very useful for learning about the molecular mechanism of various large and complex redox proteins and enzymes [1]. In the configuration called "direct electrochemistry", the enzyme is adsorbed onto a rotating electrode, electron transfer between the enzyme and the electrode is direct, and the turnover rate is simply monitored as a current. Electrochemical data have been used to gain information about virtually every step in the catalytic cycle: active site chemistry, redox-driven (in)activation, intra-molecular mass transport along channels that guide the diffusion of small molecules within the enzyme, long-range intra-molecular proton and electron transfer etc.
In this keynote lecture, I will introduce hydrogenases, the enzymes that oxidize and produce dihydrogen, and I will illustrate the applications of direct electrochemistry for studying the mechanism of hydrogenases, for learning about how they work or cease to work under adverse conditions, and for designing mutants that show improved catalytic properties.

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# Bio-sensing based on electrochemically-Gated Organic Field-Effect Transistors

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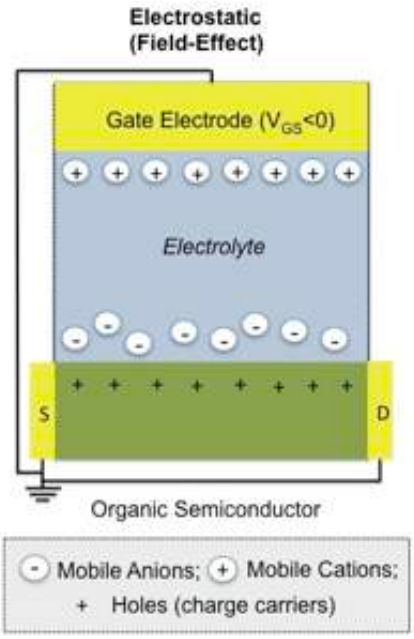
The growing demand of point of care tests along with real-time monitoring requires devices able to interface with living organism and to detect bio-chemical targets. These kinds of systems must possess i) a sensitive and selective bio-recognition system, ii) a stable operation in aqueous environment and iii) a transducing unit able to turn a biological signal into an output response.

Electrolyte-gated Organic Field-Effect Transistors (EGOFETs) represents one of the feasible configurations operating in aqueous solution. In our EGOFET setup (Fig.1), the gate/electrolyte interface, which guarantees the electrical connection with the organic semiconductor, is used as sensing core of this device that works as a potentiometric biosensor, whereas the remaining part acts as an electronic transducer.




This EGOFET turns out to be sensitive down to picomolar concentration, hence the I-V transfer characteristics show a clear decrease of the source-drain current increasing the amount of dopamine adsorbed. Two electrical parameters are sensitive: the capacitance relative to the evolution of the two in-series EDLs and the threshold voltage shift ($\Delta V_{th}$), which stems from the surface dipole at the top gate. $\Delta V_{th}$ has been fitted by a power law, which highlights how this device is more sensitive towards lower dopamine concentration[1].
This successful approach, is extremely versatile, thus it can be exploited to other systems by means of proper chemical tailoring of materials.

As a consequence, we present the first data related to the development of an electrolyte-gated field-effect transistor capable to sense Interleukin 6 (molecular weight 21,7 kDa) that is a protein involved in several inflammatory processes.
This kind of biomarker is a mediator in phase acute response and its release is associated to several pathological disorders such as diabetes, Alzheimer and prostate cancer.

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# Surface effects in routine application of ion-sensors in biomedical analysis

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The main blood electrolytes ($Na^+$, $K^+$, $Cl^-$, and $HCO_3^-$), pH and $PCO_2$ belong to the most frequently requested tests in routine clinical laboratory work [1]. These parameters are measured potentiometrically by ion-sensors located in high throughput random access analyzers. To comply with the demands of hospital laboratories (e.g. automation, reliability, traceability), medical doctors (e.g. sample volume) and/or business units (e.g. cost per test), ion-sensors have to be continually developed. For researchers, such demands call for improved and manageable response time, selectivity, and enhanced life time, as well as the need to design maintenance-free integrated sensors that allow for direct measurement in a short time and in a small sample volume.

The lecture addresses these challenges and emphasizes how the surface effects and interfacial processes may contribute to facilitating the application of ion-sensors. Two sensor surfaces will be considered: the surface in contact with the blood/urine sample and the surface acting as the internal contact, and accordingly two strategies will be presented. The first is a theoretical strategy based on the coupled Nernst-Planck-Poisson model [2], which inspects the interfacial processes and provides the benefit of a short-time non-equilibrium response. The second is an empirical one, called "solid-contact" strategy [3], in which owing to the application of conducting polymers or nanostructures, maintenance-free sensors are designed and applied in biomedical analysis.

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# Detection of nanoparticles at molecularely imprinted polymer

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In recent years, nanotechnology has been a hot topic in the scientific community due to the specific properties in the nanoscale and has become an enabling technology for numerous applications. Especially engineered nanoparticles (ENPs) have shown various beneficial properties. In many fields of application, these ENPs have left the scientific laboratories and made their way to consumer products. Beside their advantages, ENPs are under discussion in due to possible unforeseen hazards and an unknown disposition in living organisms and the environment. Nanoparticles (NPs) have drawn vast public attention due to their application in many consumer products (e.g. cosmetics, food and food packaging, drinks).

One of the key challenges is the detection, identification and quantification of engineered nanoparticles in complex matrices, such as products, food and the environment.

Here we present the first steps towards construction of a device for Point of Product Testing POPT and Point of Food Testing POFT. Molecularly imprinted polymer films were deposited on ITO-electrode surfaces. These were mounted in a "sandwich" flow cell either with two identically modified electrodes facing each other or with one polymer film modified electrode as the "floor" and a large capacitance APTMES modified electrode as the "roof". A 50 mM phosphorous buffer was used as electrolyte solution. Ag nanoparticles, diameter 9,5 nm, were flushed past the electrode surfaces at various concentrations. In order to keep the nanoparticles in solution a stabilizer was added to the stock solution.

Electrochemical impedance spectra were recorded with an amplitude of 10 mV in the frequency regime 10 MHz to 0,1 Hz and with a bias potential of 0 V between the two electrodes. Different types of molecularly imprinted polyurethane films were tested in the flow cell, both spincoated and covalently attached. Also any possible interaction with the stabilizer itself was tested.

Singular value decomposition of the impedance data made possible to perform multivariate analysis of the complex numbers (1). In the first preliminary analysis it was found that concentration levels down to 15 ng/ml could be detected.

**Acknowledgement:** The authors thank the seventh framework program for financial support; Grant agreement no: 280550 in the Instant project.

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# Interface functionnalization for efficient biological electron transfer: from enzyme orientation to biofuel cells

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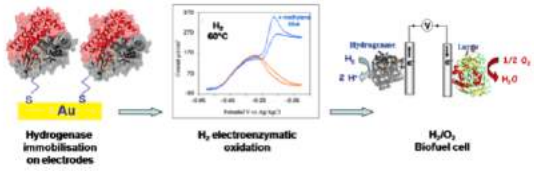
Fuel cells using renewable resources may be an interesting possibility in taking up the energy challenges launched by fossil fuel exhaustion. However they need conventional catalysts based on platinum that are available only in limited amounts, are scarcely selective and easily inhibited by many pollutants. An attractive alternative in this context might be the use of enzymes. Since more than twenty years, many biofuel cells using glucose and oxygen as a fuel and an oxidant have been developed. Recently, a new kind of biofuel cells based on dihydrogen oxidation catalyzed by hydrogenases at the anode, and on oxygen reduction by multi-copper oxidases at the cathode has emerged. Especially, [Ni-Fe] membrane-bound hydrogenases, such as that one from the hyperthermophilic organism *Aquifex aeolicus*, has recently proved to be valuable candidates in $H_2/O_2$ biofuel cells, because they oxidize hydrogen with high efficiency while presenting outstanding $O_2$, CO and temperature resistances (1).

The first step for the development of such biotechnological devices is the efficient and stable immobilization of the enzymes on the electrochemical interfaces. To raise the current densities at the electrodes and then the power densities for future $H_2/O_2$ biofuel cells, the amounts of electrically connected enzymes must be maximized. This task is still challenging because of the size of the enzymes compared to chemical catalysts, and because the active site is very often buried inside the protein moiety. For that purpose nanostructuration of the electrochemical interfaces is very attractive. One objective is to succeed in a specific orientation of the enzymes on the conductive support so that the interfacial electron transfer rate can be optimized. Alternatively, conductive supports with high surface to volume ratios like conductive polymers or porous carbon materials might be used (2-3). In this latter case, enzyme orientation limitation can be overcome thanks to the 3D-network. In this talk, the respective gains and issues for these two main research axes will be discussed, and outlook for $H_2/O_2$ biofuel cell design will be envisioned.

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# Electroanalysis of Amyloid Formation of Parkinson's Disease alpha-Synuclein

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Amyloid formation of proteins and peptides is an important biomedical and biotechnological problem, intensively studied and yet not fully understood. In this context, the development of fast and reliable methods for real-time monitoring of protein misfolding is of particular importance for unambiguous establishment of disease- , drug- and environmentally induced mechanisms of protein aggregation. Here we show that the extent of aggregation of αsynuclein (αSN), involved in Parkinson's disease and other neurodegenerative disorders, can be electrochemically monitored by oxidizing tyrosine (Tyr) residues surface-exposed in monomeric αSN and buried in fibrillated αSN adsorbed onto graphite electrodes. Adsorption of αSN was analyzed via Tyr electrochemistry (Figure 1) and followed the Langmuir adsorption isotherm. A degree of electrooxidation of Tyr in αSN decreased upon protein fibrillation and correlated with the extent of αSN aggregation determined by the spectroscopic analysis of the fibrillation process. Minor changes in the adsorption state of αSN were followed through the shift of the Tyr oxidation potential, consistent with the compact and lesscompact/unfolded conformation of αSN. Our results allow reliable electroanalysis of the extent of αSN fibrillation *in vitro* and offer an efficient tool for future *in vivo* monitoring of the protein conformational state.

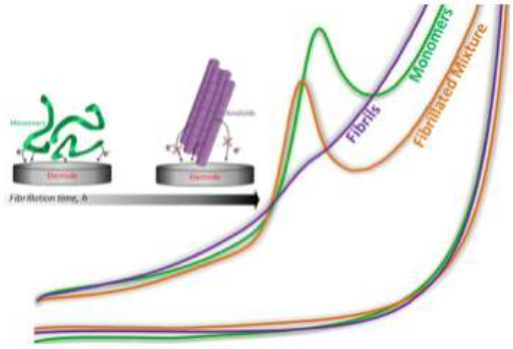


***Figure 1*** *– Electrochemical assay for analysis of the protein aggregation based on electrooxidation of Tyr residues of αSN.*

# Silver Nanowires as Plasmonic Sensor Platforms

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We describe a strategy of applying metallic silver nanowires as possible platform for plasmonically active sensors. Among numerous advantages of metallic nanowires synthesized chemically in solution are the ability to directly image them using standard optical microscopy and strong plasmonic character due to sub-micron diameters. Also important is the ability to manipulate the chemistry of the nanowire surface for requested functionality.

While depositing emitters directly on the nanowires leads to fluorescence enhancement [1-3], this is surface functionalization for conjugating the nanowires with other compatibly functionalized or active nanostructures that is the most promising. Conjugation may lead to either fluorescence enhancement or quenching, depending upon particular configuration.

We show that conjugating silver nanowires with biologically functional photosynthetic complexes results in strong increase of fluorescence intensity accompanied with shortening of the fluorescence lifetime. On the other hand, upon conjugating the silver nanowires with semiconductor nanocrystals, the emission of the nanocrystals gets reduced, as their fluorescence lifetime. While in both cases the conjugation pathway was identical, the outcome is radically different. The origin of this duality will be discussed.

Finally, we show experiments, where the concentration of biomolecules that can be viewed as an analyte, is reduced without any hampering of the performance of the plasmonic nanowire.

Financial support from the WELCOME program “Hybrid nanostructures as a stepping-stone towards efficient artificial photosynthesis” awarded by the Foundation for Polish Science and BOLDCATS project funded by the European Science Foundation is gratefully acknowledged.

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# Design of Biobattery with Enzymatic Cathode and Zinc Anode for Powering Neurotransmitter Sensor

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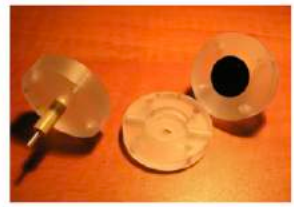
The advantages of biobatteries include easy miniaturization and utility for powering small devices e.g. sensors, switches, watches and other electronic devices [1,2]. Recently, we have shown the biobattery parameters and its application for powering a clock [3]. Our aim now is to optimize the construction of the biobattery and couple it with a biosensor for neurotransmitter detection. Arylated multiwall carbon nanotubes with bound laccase are used on the cathode for the reduction of oxygen and zinc disc covered with hopeite is the anode. Arylated carbon nanotubes increase the working surface of the electrode and provide direct contact with the active sites of laccase. The substrate is carbon sheet paper or buckypaper. The zinc – air sandwich biobattery shown below works under stationary or flow conditions. Parameters and time dependencies of the flow cell were evaluated. The system including the sandwich biobattery connected with the sensor was employed for monitoring selected neurotransmitters.

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# Effects of essential fatty acids on molecular interactions in cholesterol/phospholipid model membranes

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Among various types of amphiphilic molecules that form biological cells, essential fatty acids (EFAs) play an important role in maintaining the homeostasis of lipid membranes [1]. They occur within natural bilayers, mainly as components of phospholipid and cholesterol esters, although they can also occur as free fatty acids (FFAs) [2]. The presence of EFAs in biological membranes significantly affects the properties of natural bilayers, what makes them responsible for the synthesis and metabolism of a large variety of lipid components [3,4]. Therefore the study of interactions between selected EFAs and the main constituents of natural lipid membranes is of particular importance.

The aim of the present work was to examine the effect of selected EFAs: linoleic acid (LA), α-linolenic acid (ALA) and arachidonic acid (AA) on molecular interactions between cholesterol and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) at the air/water interface. It was possible by analysing physicochemical properties of Langmuir monolayers, treated as the simplest model of a half of a biological membrane.

Analysis of obtained results indicate that any differences in the EFAs interactions with cholesterol/DPPC model membranes are mainly related to their geometric structures. It was found that the presence of LA and ALA in the cholesterol/DPPC model systems increases the distance between lipids and weakens the repulsive interactions resulting from the steric hindrance of neighboring molecules of cholesterol, as well as reduces the repulsive interactions occur between polar groups of DPPC molecules. However, the incorporation of AA into the model membranes additionally weakens attractive van der Waals forces between the hydrocarbon chains. Thus, the introduction of even small amount of AA decreases stability of the examined systems, in contrary to LA or ALA.

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# In vivo characterization of extracellular metabolites in Pseudomonas aeruginosa cultures

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Phenazines are secondary metabolites produced by *P.aeruginosa* that are relevant to virulence, cell signaling and biofilm formation. Quorum sensing system and gene duplication confer *P. aeruginosa* great flexibility in phenazines biosynthesis in accordance with environmental conditions (1). The *Pseudomonas* quinolone signal (PQS) is the main regulator for phenazine biosynthesis in planktonic and biofilm conditions. Apart from their physiological role, phenazines are redox mediators that enable *P. aeruginosa* to convert organic carbon substrates directly into electricity in Bioelectrochemical Systems (BES) (2). However, little is known about phenazine and PQS expression in BES. It is likely that the electrode potential affects phenazine biosynthesis and their redox state. Additionally, PQS is electroactive (3), thus its concentration and redox state may be affected by electrochemical potential. *P. aeruginosa* cannot grow sustainably at an electrode maintained at oxidative potential, unless soluble electron acceptors are provided, such as oxygen or nitrate (under anaerobic conditions). The dynamic of phenazines and PQS is not known under anaerobic conditions. We hypothesized that anodic potential determines the expression of redox-active metabolites when *P. aeruginosa* is grown in potentiostat-controlled electrochemical cells (ECs). To prove our hypothesis, *P.aeruginosa* and key mutants with minimal phenazine and PQS biosynthesis were characterized in anodic ECs by amperometric and voltammetric methods. Results show that phenazine concentration increases as anodic potential decreases from 0.4 V to -0.2 V vs. Ag/AgCl. This result indicates that overproduction of phenazines allows *P. aeruginosa* to transfer electrons to the anode under unfavorable redox conditions, thus providing a competitive advantage over other microorganisms in the consortium. Additionally, PQS concentration increase as the potential decreases and PQS is rapidly secreted when the cells are exposed to anaerobic conditions, suggesting that PQS may work as alternative electron acceptor in lack of oxygen and other efficient electron acceptors.

We have monitored for the first time the production of redox-active metabolites in viable cultures of *P. aeruginosa*. Our results contribute to unveil the complexity of electroactive species produced by *P. aeruginosa* and grant further research on the effect of electrode potential on viable microbial cultures and biofilms.

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# Lignosulfonate-Stabilized Nanoparticles: Proparation and Electrochemistry

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The application of biorenewable materials in the design and development of advanced materials has been the area of rapidly increasing patent and literature activity. Lignosulfonates (LSs) are sulfonated derivatives of parent lignin which is the second (after cellulose) most abundant biopolymer found mainly in wood and grass. They are produced as by-products of chemical pulping of wood during making of paper. From the chemical structure point of view, lignosulfonates are easily oxidizable, amphiphilic polymers showing surfactant properties. Previously, we have shown that LSs can be electrochemically converted to a redox active quinone-containing biopolymer when adsorbed on the surface of carbon electrode [1] or introduced into electrochemically grown poly-pyrrole [2] or PEDOT [3].

In this presentation, the chemical structure of lignin and lignosulfonates will be briefly discussed. More attention will be put on how LSs can be used in preparation of various nanoparticles such as: silver, gold, selenium and hexacyanometalates. The examples of applications presented will provide a brief overview of spectrophotometric chemical sensing based on silver and gold nanoparticles, Raman spectroscopy on nanostructured surfaces based on LS-stabilized silver and gold nanoparticles (SERS) and electrocatalysis. Additionally various methods for immobilization of the prepared nanoparticles on electrode surfaces will be discussed. For instance silver nanoparticles synthesized with the aid of softwood lignosulfonate [4] can be readily and effectively introduced into zinc oxide electrodeposited by cathodic reduction of aqueous $Zn(NO_3)_2$ solution.

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# Electrochemical screening of biomembrane-active compounds in water

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Interactions of biomembrane-active compounds with phospholipid monolayers on microfabricated Pt/Hg electrodes in an on-line high throughput flow system are demonstrated by recording capacitance current peak changes in rapid cyclic voltammograms (RCV). Detection limits of the compounds' effects on the layer have been estimated from the data. Compounds studied include steroids, polycyclic aromatic hydrocarbons, tricyclic antidepressants and tricyclic phenothiazines. The results show that the extent and type of interaction depends on the: - (a) presence and number of aromatic rings and substituents, (b) presence and composition of side chains and, (c) molecular shape. Interaction is only indirectly related to compound hydrophobicity. For a selection of tricyclic antidepressants and tricyclic phenothiazines the detection limit in water is related to their therapeutic normal threshold. The sensing assay has been tested in the presence of humic acid as a potential interferent and in a tap water matrix. The system can be applied to the screening of putative hazardous substances allowing for early detection thereof in the water supply. The measurements are made in real time which means that potentially toxic compounds are detected rapidly in <10 minutes per assay. This technology will contribute greatly to environment safety and health.

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# Application of zeolite - type cesium salt of heterpolytungstic as supports for catalytics center towards electrooxidation of alcohols

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Direct alcohol fuel cells (DAFCs) are considered as an alternative energy source. The alcohols that are used as fuel in DAFCs are methanol, ethanol, ethylene glycol and 2-propanol. Liquid fuels, such as small molecular weight alcohols and formic acid together with their esters with high volumetric energy density and better energy efficiency, are easier to store and transport in comparison to hydrogen or other gaseous fuels. In order to increase the fuel utilization and the fuel cell efficiency, it is important to break C-C bond and cause its complete oxidation into carbon dioxide $CO_2$. Platinum is recognized as the most active catalytic metal towards oxidation of alcohols (1). However, Pt anodes are poisoned by the strongly adsorbed intermediates (CO, CHO), requiring high overpotentials for their removal (2). Enhancement of the catalytic activity may be achieved also by modification of platinum surface with another metals (Sn, Rh, W, Ru), metal oxides ($WO_3$) or polyoxometallates (3-7). In our study, we propose modification of platinum-based catalysts (PtSn/Vulcan XC-72, PtRh/Vulcan XC-72) with zeolite-type cesium salts of heterpolytungstic acid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. This salt is insoluble in water and organic solvents, and it possess micro- and mesopores of high surface area. It has also been reported (8) that cesium salts of Keggin-type heterpolymolybdates and heterpolytungstates can be active support for noble metal nanoparticles towards electrooxidation of ethanol. Modification of platinum-based catalysts with cesium salts of heterpolytungstic acid results in the enhancement of their electrocatalytic properties towards electrooxidation of 2-propanol, as demonstrated in terms of the increase of the respective voltammetric and amperometric catalytic currents.

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# Enantioselective electrodes based on inherently chiral molecular materials

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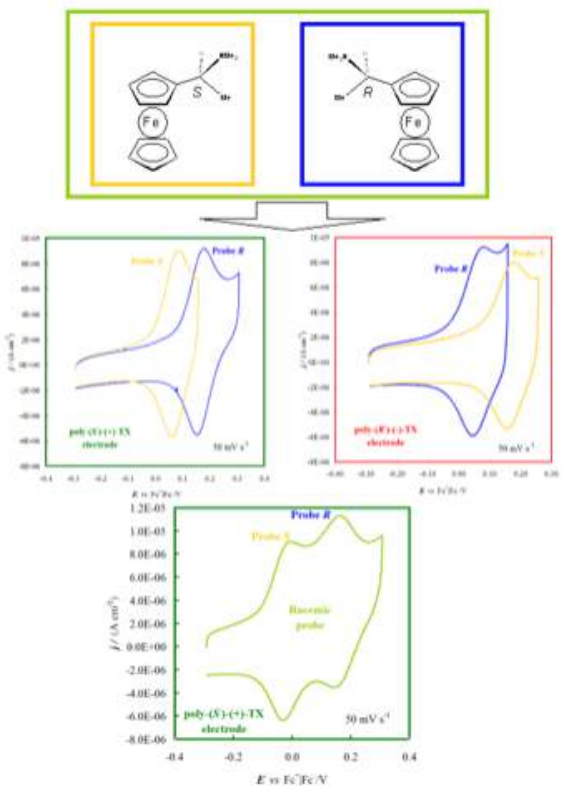
Materials coupling electroactivity with enantiorecognition capability are an attractive objective in current research. The usual strategy, hinging on attaching chiral pendants to an electroactive polyconjugated backbone, generally results in modest chirality manifestations. We have designed electroactive chiral polyheterocycles, where chirality is not external to the electroactive backbone, but inherent to it, resulting from a tailored torsion produced by the periodical presence of atropisomeric, conjugatively active biheteroaromatic scaffolds.




This affords enantiopure electroactive films of impressive chiroptical activity; moreover, since the stereogenic element coincides with the electroactive site, chirality manifestations can be finely and reversibly tuned by the electric potential, since progressive injection of positive charges forces the atropisomeric scaffold angle to regularly decrease to favour delocalization. Such deformations are elastic and reversible (CD spectroelectrochemistry). In order to test the enantiorecognition ability of the new enantiomeric electrodes, we have in the last months developed a protocol in ionic liquid medium affording preparation of very reproducible electrode surfaces on screen-printed electrode supports.

The resulting specular R and S electrodes have been tested in the presence of (R)-(+)- and S-(−)-N,N-dimethyl-1-ferrocenylethylamine specular probes. The response is highly and reproducibly enantioselective (even more than 100 mV separation between R and S probes, either with single enantiomers and with the racemate), specular for R *vs* S surfaces with respect to S and R probes, and reversible in repeated alternating sequences of S and R probe sensing on a single electrode. Similar results have been obtained applying the

# Biomembrane-based biosensors: a revolution in analytical chemistry

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Up to 40 years ago both bioanalytical and environmental analytical science focused on measuring the exact and precise concentration of a component and its species in a medium. Concerns at the time were raised on the biological relevance of these measurements and how they related to both the biological activity and the bioavailability of the determinand. In order to address this issue, inspiration was sought from biological taste and smell mechanisms which in many cases provided for a more relevant measure of the active form of a species. The concept of the biosensor was therefore born which transferred the biological sensing mechanisms to a biological sensing element so that the sensing process could be measured by some transduction mechanism usually electronic or optical.

The biomembrane is the most critical interface in living organisms since not only does it form an impermeable boundary to a living cell but its structure is host to numerous physiological processes within the cell. It is therefore sensitive to many potential analytes and is an obvious choice to use as a sensing element in a biosensor. This tutorial lecture will describe the development of the biomembrane-based biosensor from the first lipid bilayer devices to the modern range of membrane-based biosensors using all the tools of nanotechnology. These sensing technologies which use both natural and artificial biological membranes as sensing elements have been explored for over twenty years. Their development is justified by their high sensitivity and specificity for biological membrane active species. A wide variety of membrane based sensors are under development worldwide, including tethered bilayers[1], suspended bilayers[2] and hybrid layers[3] all of which incorporate a protein receptor or ion channel within the membrane. Detection of the analyte of interest is achieved following binding of the analyte with the protein receptor or ion channel[4], which is often measured using faradaic or conductive processes. A different approach uses membrane-like layers physically adsorbed to a metal[5]. These systems have the following advantages over the alternatives: simplicity, unique mode of action, relevant platform and broad selectivity. They were developed from classical interfacial electrochemical studies of the adsorption of organic compounds on to electrified conducting metal surfaces[5]. In the final analysis a successful sensing system which can be commercialised has to be robust, rapid and sustainable. The lecture will conclude by describing some successful membrane-based sensing systems with interesting applications for example in nanotoxicology[6].

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# Studies of rate of deposition of actives on cellulose modified surfaces using Electrochemical Quartz Crystal Microbalance

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Electrochemical Quartz Crystal Microbalance (EQCM) is a powerful technique employed in the study of nanoscale changes in mass and electrochemical measurements at an electrode surface simultaneously. It utilizes the reverse piezo-electric effect to compute the changes in frequency on an AT-cut crystal surface. This is translated to changes in mass using the Sauerbrey equation (Equation 1), where $\Delta f$ *is* change in frequency, $f_o$ is the fundamental frequency of an AT-cut crystal, A, $\varrho_q$ and $\mu_q$ is the active area, density and shear modulus of the crystal and $\Delta m$ is the change of mass.

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}} \cdot \Delta m$$

EQCM applications include studies of underpotential deposition, ion transportation and determination of point of zero charge[1,2,3]. This project uses EQCM to study the kinetics of deposition of active substances on model cellulose surfaces. A 6MHz gold-coated quartz crystal is used. Cyclic voltammetry measurements are recorded simultaneously. The gold-coated surface serves as a working electrode for the electrochemical measurements together with an Ag/AgCl and a gold electrode as a reference and counter electrodes respectively.

Keywords: EQCM, cellulose modification, deposition, cyclic voltammetry.

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# Interactions of Doxorubicin with Organized Interfacial Assemblies

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Doxorubicin is an anthracycline, cytostatic antibiotic, which is widely used in the cancer treatment. The mechanism of drug crossing through the lipid bilayer in cells is still unknown, therefore it's very important to study the transport of doxorubicin through the membranes. The aim of this work is to investigate the permeation of doxorubicin through model membrane system. We have studied interactions between doxorubicin and Langmuir/Langmuir-Blodgett monomolecular films of, dihexadecylphosphate (DHP) and 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), and two types of DMPC bilayer films on solid substrate: gold and mica. The way of doxorubicin penetration through biomembranes was measured with using, Langmuir method, Brewster angle microscopy and spectroscopic technigues: Surface Enhanced Raman spectroscopy (SERS) and Flim microscopy. For all biomimetic films there is a substantial interaction between doxorubicin and the interface, and the extent of this interaction depends on the hydrophobic/hydrophilic properties of the film formed and its organization. The measurements show that the drug adsorbs easily on the hydrophilic part of the monolayer. The hydrophobic part allows for the penetration and accumulation of the drug within the monolayer moiety, while its organization controls the rate and amount of DOX partitioning through such kind of films.

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# Chronopotentiometric analysis of proteins, polyamino acids and peptides

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Electrochemistry of a relatively small number of conjugated proteins containing non-protein redox centers, reached in recent decades a highly sophisticated level but only little attention was paid to electrochemistry of thousands of proteins important in proteomics and biomedicine. Recently we have shown that using constant current chronopotentiometric stripping (CPS) in combination with mercury-containing electrodes practically all proteins produce electrocatalytic peak H (1,2) due to catalytic hydrogen evolution. Proteins can be determined down to nM and subnanomolar concentrations, using peak H at low current densities. At higher current densities CPS protein structure-sensitive analysis was developed. At thiol-modified electrodes, changes in properties of mutant proteins resulting from single amino acid exchange are in excellent correlation with structural and stability data (3,4). Enzymatic activity of urease attached to bare or thiol-modified SAEs at open circuit potential was retained while prolonged exposition of the enzyme to negative potentials resulted in the enzyme denaturation. In spite of great importance and usefulness of the CPS analysis, the role of individual aa residues in the catalytical hydrogen evolution of proteins has not been yet fully understood. We showed that arginine, lysine and histidine residues in homo poly(amino acids) and peptides contribute to catalysis of hydrogen evolution close to physiological conditions (5,6). Peak potentials of individual poly(amino acids) are different and depend on the type of the amino acid residues.

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# Electrochemical biosensing platforms for miRNA detection

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MicroRNAs (miRNAs) are intensely studied as candidates for diagnostic and prognostic biomarkers. They are naturally occurring small RNAs (approximately 22 nucleotides in length) that act as regulators of protein translation. Because many diseases are caused by the misregulated activity of proteins, miRNAs have been implicated in a number of diseases including a broad range of cancers, heart diseases, immunological and neurological diseases. miRNAs are more stable, due to their small size as compared to long mRNA. They can be extracted and detected from cells and tissues, blood (either total blood, plasma or serum) circulating exosomes and from different biological fluids like urine and even sputum. These info support their possible use as novel, minimally invasive and robust biomarkers. Almost entirely due to their short size, the analysis of miRNAs is considerably more difficult than it is for much longer mRNAs. In particular, the small size of miRNAs greatly complicates the use of standard biology methods based on PCR. A great deal of effort, therefore, has been devoted to develop new analytical methods for miRNA analysis. Electrochemical biosensors have long been viewed as attractive for nucleic acid analysis. In this context, different approaches have been proposed for miRNA analysis in the literature. Electrochemical techniques, such as faradic impedance spectroscopy, chronoamperometry, scanning electrochemistry microscopy and differential pulse voltammetry, have been used by our group, for the development and characterization of biosensors for miRNAs detection. 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. Dendritic-type amplification of a target miRNA has been also accomplished by the use of streptavidin and biotinylated alkaline phosphatase, which can be self-assembled to build nanoarchitectures rich in enzyme label. The detection of miRNAs in cancer cells has been performed and results here reported.

# High redox potential blue multicopper oxidases adsorbed on bare gold surface

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Two blue multicopper oxidases (MCOs), *viz*. *Trametes hirsuta* laccase (*Th*Lc) and *Myrothecium verrucaria* bilirubin oxidase (*Mv*BOx), were immobilised on bare polycrystalline gold (Au) surfaces by direct adsorption from both diluted and concentrated enzyme solutions. The adsorption was studied *in situ* by means of null ellipsometry. Moreover, the biomodified gold electrodes were investigated in detail by atomic force microscopy (AFM), as well as electrochemically. Depending on the method and protein concentration used for immobilisation, the amount of enzyme per unit area was determined to be *ca*. 1.67 and 4.83 pmol $cm^{-2}$ for *Th*Lc and *Mv*BOx, respectively, whereas protein film thickness was calculated to be 29 and 30 Å for *Th*Lc and *Mv*BOx, respectively. A well-pronounced bioelectrocatalytic reduction of oxygen, which depends on the experimental conditions[1], was observed on *Mv*BOx/Au biocathodes whereas this was not the case for *Th*Lc modified Au electrodes in spite of the well pronounced biocatalytic response on modified, *e.g*. thiol protected[2], Au surfaces. Irreversible denaturation of MCOs on polycrystalline Au electrodes, in all likelihood due to the flattening of enzymes on bare Au surface, was suggested to explain the observed experimental results.

The work has been financially supported financially by the Russian Foundation for Basic Research (research project ? 12-04-33102) and by the Faculty of Health and Society, Malmö University, Sweden.

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# Nanostructured films of in situ deprotected thioacetyl functionalized C60-fullerenes on gold electrodes

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The electronic properties of fullerenes make them extremely attractive from the electrochemical and photochemical point of view. For example, the ability of $C_{60}$ to be reduced reversibly with up to six electrons has led to the synthesis of a large number of donor-acceptor systems in which it acts as an electron acceptor (1). Because of this electron-accepting feature, $C_{60}$ components have been considered for various practical applications including photovoltaic devices (2), superconductors (3), and field effect transistors (4).

In our work $C_{60}$ molecules have been functionalized according to the Prato method with the S-acetyl-protected chains (Figure 1). The compounds were deposited at gold electrodes by self-assembly following an *in-situ* deprotection procedure which transformed the thioacetyl-functionalized compounds into their thiolated derivatives. LUMO-HOMO band gaps obtained from the electrochemical data were compared with the DFT theoretical values for the optimized structures. The thioacetyl-functionalized $C_{60}$ derivatives were employed for the catalytic reduction of halogenated hydrocarbons. Following deprotection, they were employed for the modification of gold substrates. Solvent dependent barrier properties of the thiolated fullerene films were investigated by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The topography of $C_{60}$ derivative modified electrode investigated by XPS and AFM confirmed stable modification of the Au support with a 3-D film of fullerene worm-like aggregates.

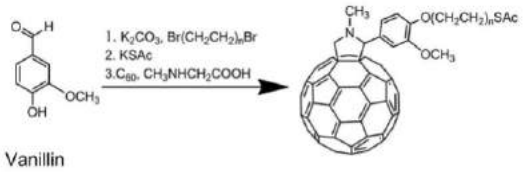


***Figure 1.*** *The general method for preparation of thioacetyl-functionalized $C_{60}$-fullerenes films on gold surface (n=1,3,6).*

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# Pore formation and lateral disruption of lipid membranes in response to action of bee venom toxin

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A wide range of relatively simple peptides, both synthetic and naturally occurring, interact dynamically with lipid bilayers. Many mono- or multicellular organisms secrete soluble proteins, referred to as protein toxins, which alter the behavior of foreign, or target cells, possibly leading to their death.[1] The mode of action of toxins can be very diverse. However, considerable group exhibits pore-forming action on cell membranes. Melittin is a representative example. It is a water-soluble amphipathic helical peptide of 26 amino acids activity isolated from the honeybee *Apis mellifera*. Melittin has strong hemolitic activity. It binds to erythrocytes where the peptide causes an increase in permeability for alkali metal ions, resulting in cell swelling and release of hemoglobin[2]. Melittin shows a wide range of possibilities to interact with biological as well as artificial membranes, e.g. it causes hemolysis of cells and leakage of entrapped dyes in lipid vesicles, it induces bilayer micellation and fusion, and it shows voltage-gated channel formation[3]. Therefore melittin is a suitable and interesting model for the investigation of protein interactions with prepared solid supported membranes.

The interaction of the membrane active peptide melittin with solid supported lipid bilayers composed of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and N-(hexadecanoyl)-sphing-4-enine-1-phosphocholine (HSM) and cholesterol (CHOL) on mica has been scrutinized using atomic force microscopy (AFM). First, AFM imaging of supported membranes was performed to provide nanometer-scale information on membrane topography and thickness.. Melittin-lipid interaction behaviour is complex with both pore-forming and 'detergent-like' effects, dependent on peptide:lipid ratio. It was confirmed by AFM examination of solid supported lipid bilayers in presence various concentrations of melittin. Changes in bilayers structure at low concentration of melittin included transmembrane pores formation and distortion of phosphocholine bilayer matrix (while imaging, the lipids partially dissolve, leaving behind a textured structure which exhibits a large number of small linear defects). The examination of the bilayer at higher concentrations of melittinrevealed that peptide disturbs the membrane to large extent resulting in formation of large defects or total destruction of the film. Interestingly, only phosphocholine rich (DOPC) parts of membrane were destroyed and the HSM/CHOL lipid domains remained intact even at high concentration of melittin.

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# Carbon nanotubes based electrochemical aptasensing platform for applications in human blood serum

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Electrochemical aptasensors have attracted great attention due to their high sensitivity and selectivity, as well as a low fabrication cost [1]. By combining the inherent properties of nanomaterials with the specific recognition ability of aptamers (single stranded DNA), a range of nanomaterial (NM)–aptamer conjugates have shown their utility for different analytical purposes. Between vaious NMs, carbon nanotubes (CNTs) have received attention due to their unique chemical, mechanical and electronic properties such as high chemical and thermal stability, as well as high surface area. In the present study, a sensitive and selective electrochemical biosensor has been developed based on the covalent attachment of the aminated aptamer on carboxylated mulitwalled CNTs (MWCNT) for the sensitive and selective detection of hydroxylated polychlorinated biphenyls (OH-PCBs).

Polychlorinated biphenyls (PCBs) are known as endocrine disruptors which are highly persistent and lipophilic, and could transfer to a higher level through the food chain. In the body, PCBs can metabolize to OH-PCBs by the oxidative metabolism of cytochrome P450 monooxygenases and can disturb thyroid hormone homeostasis. The OH-PCB's high lipophilicity and affinity to certain proteins such as the thyroxin-transporting protein transthyretin lead to the retention of OH–PCB in different body parts, mainly in blood. Therefore, it is important for toxicological studies to determine the presence of OH-PCB in human blood samples.

As a consequence, in this study, the analytical performance of sensing OH-PCB has greatly improved by using the described aptasensor.The developed aptasensing platform was characterized by Electrochemical Impedance Spectroscopy (EIS), Atomic Force Microscopy (AFM) and Fourier transform Infrared Spectroscopy (FTIR). The obtained results suggest that the designed electrochemical aptasensing device can be used in the field of biomonitoring with high sensitivity and selectivity with acceptable stability in human blood serum samples.

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# Plastic antibodies

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Molecularly Imprinted Polymers (MIPs) are generic alternatives to antibodies and natural receptors in diagnostics and in separation. Here we report an efficient and flexible method for automatic synthesis of MIP nanoparticles using solid-phase automated photo/chemical reactor. Our approach requires a cartridge with an immobilised template docked into a thermostatic computer-controllable reactor, thereby allowing controlled manufacturing of affinity nanoparticles with narrow size distributions in the range 20-400 nm. We demonstrate the synthesis of water-soluble affinity nanoparticles for various targets such as melamine, vancomycin, peptides, proteins and virus particles with minimal manual intervention and short reaction-cycle times. The developed reactor allows easy functionalisation of nanoparticles with fluorescent, electrochemical or magnetic labels. The affinity of all synthesised nanoparticles is at the picomolar-nanomolar level which makes them suitable for practical applications in assays, sensors and in affinity chromatography. The synthesised nanoparticles also possess bioactive properties. Thus specific MIP nanoparticles made for enzymes are capable of activating or inhibiting enzyme activity, depending on binding mechanism. With this new development in MIP synthesis we foresee a time when the application of natural antibodies in diagnostics would be challenged by appearance of new sensor devices and assays that utilize stable and inexpensive "plastic antibodies" with integrated recognition and signalling functionalities. Equally exciting could be *in vivo* applications for such materials which would be discussed in the present paper.

# Chemoselectivity in Integral and Local Electrode Surface Modificatio

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Biochemical sensing often rely on surface tethered (bio)-recognition elements. The thiol-gold interaction is the predominant strategy and has the advantage of a well-defined surface chemistry. However, due to limitations in the choice of materials as well as in stability, especially for electrochemical applications, alternative approaches based on electrografting of phenyl diazonium cations have been developed (1). While the stability improvement is undisputed, the nature of the bonding between the modifying film and the electrode surface as well as the structure of the film often remains unclear.

The electrografting of phenyl diazonium salts on electrode materials may yield monolayer (2) or multilayer films. Strategies for controlling the film thickness will be proposed. In the particular case of the gold surface, evidences for the nature of the bond between the gold and the organic film will be presented and compared to the one obtained from alternative surface modification strategies on gold.

Elucidation of the surface chemistry becomes even more challenging when the surface modification is performed locally for patterning applications. The chemoselectivity of electropatterning methods will be discussed with particular focus on various direct mode SECM based approaches. Evidence for chemoselective surface patterning will be presented and discussed (3).

Acknowledgement: financial support by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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# Modification of the liquid ? liquid interface with surfactant-templated silica materials by ion transfer voltammetry

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This study is at the confluence of Sol-Gel processes of silica and of the electrochemistry at Interface between Two Immiscible Electrolyte Solutions (ITIES). In electrochemistry it is convenient to compare the ITIES with the working electrode from a traditional electrochemical set up. In contrast to solid state electrodes, the detection at ITIES is not restricted to electron transfer reactions. Electrochemistry at ITIES can be exploited for the determination of various ionic analytes, ranging from inorganic molecules (1) to organic compounds (2) and even to biologically important species (3). Unfortunately, the ITIES sensors are not flawless. With good sensitivity and high limit of detection they are still suffering from lack of selectivity. One of the ways to improve this parameter is the liquid-liquid interface modification with the material that possesses sieving properties. Clearly, Sol-Gel-derived silica materials could provide such properties of interest. Additionally, under proper conditions one can control the morphology of silica films on electrodes as it was reported for the electro-assisted self-assembly (4) method.

Our objective is to modify the liquid-liquid interface with a surfactant-templated mesoporous silica membrane. The system studied consists of an aqueous solution of hydrolyzed silica precursor and an organic solution of template salt (cationic surfactant). By cyclic voltammetry, we control the transfer of surfactant molecules to the aqueous phase. The result of the reaction between template and precursor is a surfactant-templated mesoporous silica film generated at the interface. In this study, we optimized the experimental conditions (precursor and template concentrations, ratio of the two components, scan rates, compositions of the aqueous and organic phases…) of the *in situ* film formation at a macroscopic ITIES. After deposition, silica films were collected from the interface and analyzed by Infra-Red and X-ray Photoelectron Spectroscopies. Small Angle X-ray Spectroscopy analyses indicate the short-distance symmetry of worm-like type confirmed by Transmission Electron Microscopy.

Second part of these work belong to miniaturization. In recent years, processes occurring at the miniaturized ITIES have been widely studied (3). Application of micro or nano ITIES entails two main features which are improved sensitivity due to enhanced mass transport and higher limit of the detection as a reason of small capacitance current. $\mu$ITIES were thus modified by ion transfer voltammetry as above, and analysed with Scanning Electron Microscopy, Raman and Infra-Red spectroscopies. Finally modified interfacial sensors were tested electrochemically with some model ions (tetraalkylammonium cations, hemoglobin and 4-Octylbenzenesulfonic acid) of various charges and sizes.

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# Voltammetric determination of lead and cadmium using plant refuses modified carbon paste electrode

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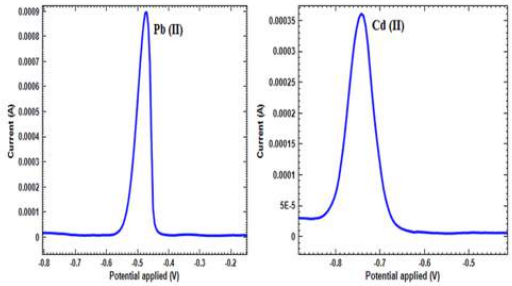
The present work deals with the modification of Carbon paste electrode (CPE) with *Citrus limon* peel to enhance its activity toward metal determination in aqueous samples. The prepared electrode was characterized using cyclic voltammetry, electrochemical impedance spectroscopy study and AFM. Differential pulse stripping voltammetry was utilized to characterize the electrochemical parameters and the performance of this new metal sensor under different preparation and operation conditions. Metal ions were pre-concentrated on the modified electrode surface at open circuit and determination of these metal ions was carried out by stripping voltammetry in anodic direction. Different operational conditions were optimized for determination of lead and cadmium. The effect of surface active macro molecules was also studied. Enhancement in metal detection and determination has been observed with the modified electrode for Pb (II) and Cd (II) as compared to the bare CPE. Differential pulse anodic stripping voltammogram for the determination of Pb (II) and Cd (II) are shown in the figure. The limit of detection values observed are 59.5 ppb and 64.4 ppb for Pb (II) and Cd (II) respectively.



# Estimation of sorption properties of the algae Spirogyra sp

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The capacity of heavy metal sorption by algae used for *in situ* study depends on the abiotic factors, eg. water pH and the presence of other cations naturally present in water ecosystems.

In order to assess the algae sorption properties and the effect of other factors on the sorption equilibria, the sorption properties of freshwater algae *Spirogyra* sp. were studied in the laboratory conditions. Saline solutions of the following heavy metals: Mn, Cu, Zn and Cd were used for the study. The heavy metals affinity, determined on the basis of the conduced analyses, with the thallus of algae *Spirogyra* sp. increases in the following sequence: $Cd^{2+} < Mn^{2+} \approx Zn^{2+} < Cu^{2+}$. It was reported that the sorption competitiveness of the cations naturally present in the algae habitat in relation to $Mn^{2+}$ ions changes in the following series: $Na^{+} < Ca^{2+} < H^{+}$ determined for concentrations referred to ion unit charge.

The model of Langmuir isotherm was used to describe equilibriums. The carried out tests confirmed that 30 min of exposition of algae slightly polluted by heavy metals in water contaminated eg. by manganese ions, results in increase in concentration of these ions in algae thallus, proportionally to their concentration in the tested water. It was also found that the presence of other ions in solution cause statistically significant changes in the slope of the Langmuir isotherm: $a = (c_{(a,max)} \cdot K)^{-1}$.

The conducted study is a part of the scientific project, the aim of which is to develop classification method of surface waters on the basis of the chemical composition analysis of algae thalli.

ACKNOWLEDGEMENTS

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# The Effect of Platinum Surface Treatment on Detection of Hydrogen Peroxide

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Detection of hydrogen peroxide as an important analyte in clinical diagnosis and chemical warfare has attracted a lot of attention. Hydrogen peroxide is considered to be a marker of oxidative stress, cancer, and Parkinson's and Alzheimer's diseases. Hydrogen peroxide is also a by-product of several enzymatic reactions and thus is used as a diagnostic marker for the detection of metabolites such as glucose and lactate. Thus, direct or indirect detection of hydrogen peroxide is important in the design and fabrication of various biosensors.

Platinum has long been used as a suitable material for the detection of hydrogen peroxide [1-3] due to its electrocatalytic properties. However, there are evidences that the oxidation of platinum surface greatly enhances its electrocatalytic properties and thus lower and extend the detection limit of the related sensors. Here, we treat the platinum surface using different oxidation methods such as ICP (samples were subjected to inductively coupled plasma) and TEPLA (samples were subjected to oxygen plasma in a Tepla 300 plasma processor). Then, we characterize these surfaces using common model redox systems and afterwards compare the electrocatalytic properties of these surfaces toward oxidation of hydrogen peroxide with those prepared using lab-bench plasma instrument, electrochemical oxidation, and untreated platinum surfaces.

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# Photoelectrochemical water oxidation with photosystem II and bio-inspired hybrid materials

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The sunlight-driven splitting of water into $H_2$ and $O_2$ represents a sustainable route for the production of the energy vector, $H_2$. We have recently made some progress in the integration of catalysts in metal oxides for electro- and photocatalytic $H_2$ generation,[1] but a fuel forming reductive process such as $H_2$ evolution can only operate in a sustainable redox cycle if electrons are provided from an oxidative process such as water oxidation to $O_2$. Nature's water oxidising enzyme, photosystem II (PSII), sets a benchmark in terms of $O_2$ evolution rates and serves as an inspiration to develop synthetic water oxidation photocatalysts. We adsorbed PSII from *Thermosynechococcus elongatus* on a nanostructured and transparent metal oxide electrode for visible light driven water oxidation to $O_2$ and observed direct electron transfer at the enzyme-electrode interface (Figure 1).[2] We have also developed a rational strategy to electrostatically orient and covalently immobilise PSII on the nanostructured electrode, resulting in an enhanced photocurrent response and film stability.[3] A straightforward method will also be presented to assemble a purely synthetic, PSII-inspired water oxidation photocatalyst based on a metal oxide nanocomposite system.[4]

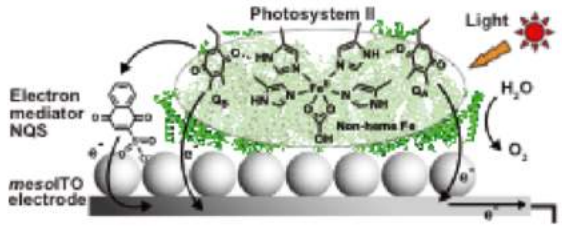


***Figure 1.*** *Schematic representation of visible light driven water oxidation with photosystem II integrated in a nanostructured indium tin oxide (ITO) electrode.*[2]

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# Imaging of mechanical properties of soft matter at nanoscale resolution by AFM: From Heterogeneous Polymer Surfaces to Single Biomolecules

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Atomic force microscopy (AFM) has become a true enabling platform in soft matter science, and specifically in macromolecular nanotechnology, including biological systems (1). Despite the tremendous progress in AFM technology development it has remained notoriously difficult to obtain quantitative mechanical maps of the elastic performance of soft matter with high resolution. Tapping mode imaging was a pivotal development in AFM technology and became a routinely used imaging mode to study polymer surfaces, allowing gentle scanning with significantly reduced lateral forces. However, it has not allowed one to obtain quantitative mechanical maps because the phase signal is related to the energy dissipation of the tapping tip (2). Despite the remarkable progress in the development of the AFM based mechanical imaging technology including commercial availability, a number of physical aspects must be addressed in the future and taken into careful consideration: effects of surface roughness and frequency of probing, the choice of the appropriate contact mechanics model and the potential impact of the underlying hard substrate if thin films are investigated.

The feasibility of peak force tapping AFM to obtain mechanical maps on a variety of polymer surfaces and biological samples down to single molecules will be discussed in this lecture (3). In addition, simultaneous current sensing with up to sub pA sensitivity enables the nanoscale electrical characterization of composites.

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# Design of optimized redox polymers. Applications for biofuel cells and photobioelectrochemistry

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Redox polymers are frequently used for wiring biological recognition elements such as e.g. enzymes with electrode surfaces. In contrast to direct electron transfer strategies from a monolayer of orientated enzymes at a suitable electrode surface redox polymers allow for the integration of a substantially higher amount of productively wired enzyme on the electrode surface. Evidently, for the design of biofuel cells or biobatteries the adaptation of the redox potential of the polymer bound redox species to the formal potential of the prosthetic group in the active site of the enzyme is of high importance. Moreover, the polymer backbone structure has to be modified to allow for high mobility of the polymer-bound redox relays, swelling of the hydrogel etc. The following aspects will be discussed:

Principles of mediated electron transfer using redox polymers and design of biofuel cells and photobioelectrochemical energy harvesting devices

Possible enzymes for bioanaodes and biocathodes for biofuel cells including the structure and possible electron transfer pathways

Synthesis of Os-complex modified redox polymers for wiring of laccases and bilirubin oxidase

Synthesis of Os-complex and phenothiazine-modified redox polymers for wiring of cellobiose dehydrogenase, glucose oxidase and PQQ-dependent glucose dehydrogenase

Design of photobioelectrochemical devises based on photosystem 1 and photosystem 2

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# Preparation and application of aptamer-modified water soluble quantum dots for detection of pathogens

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Rapid, selective and sensitive detection of pathogens is essential for medical technology, disease control and food safety. Traditional methods for pathogen detection are polymerase chain reaction (PCR), fluorescence-based assays, culture and colony counting. In this context, biosensors offer several advantages like high-throughput screening, improved detectability, label-free detection, real-time analysis over existing techniques [1]. Various types of biological molecules such as enzymes, microorganisms, antibodies and DNA can be used to fabricate biosensors. Among of them antibodies and newly aptamers has been great attention to construct pathogen detection technologies. Antibody-based sensors permit the rapid and sensitive analysis of a range of pathogens and associated toxins [2]. Aptamers are short oligonucleotides that are capable to selectively bind their corresponding target. Therefore, they can be thought of as nucleic acid-based alternative to antibodies. The design of aptamers is simple and takes short time, however antibodies are expensive and their preparation takes long time.

Herein, we report the design aptamer-modified quantum dot conjugates for detection of microbial pathogens. To perform active pathogen binding, thioglycolic acid coated quantum dots were modified with amino functional specific aptamer via EDC/NHS method. Fluorescence spectra, TEM, hydrodynamic light scattering and agarose gel electrophoresis studies show that the synthesized aptamer-quantum dot nanoconjugates were conjugated successfully. To achieve detection of microbial pathogens, electrochemical biosensor systems will be constructed and selected pathogen microorganism *Escherichia coli* O157:H7 will be determined with constructed nanoconjugate immobilized system.

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# Surface enhanced sensing with macro porous molecularly imprinted polymer film for selective arabitol recognition

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Molecular imprinting in polymers is a well-established procedure for preparing artificial recognition units of chemical sensors. Using this procedure, one can produce materials of selectivity comparable to that of their biological counterparts. Deposition of a thin film of a molecularly imprinted polymer (MIP), playing a role of the recognition unit, directly on surface of the transduction unit integrates these units to result in a complete chemical sensor. However, if the deposited MIP film is smooth and continuous then sensitivity of the devised chemosensor is limited because of slow diffusion of analytes through the film to less accessible imprinted molecular cavities in the film bulk. Additionally, specific surface area of such a film is low. Therefore, this area should be increased, in a controllable way, for enhancement of the analytical signal. To prove the effect of surface enlargement on the resulting signal, we choose a sugar alcohol, such as arabitol, as a model template. Toward that, here, we report on electropolymerized porous MIP films prepared using silica colloidal nanoparticles (NPs) as sacrificial templates. Briefly, our procedure comprised two steps. The first step involved assembling silica NPs onto surface of an Au–film coated quartz crystal resonator via the Langmuir–Blodgett technique. The second step consisted in potentiodynamic electropolymerization of the pre-polymerization complex of arabitol with the functional monomer, in the presence of a cross-linker, leading to deposition of the MIP film. 2,2'-Bithiophene derivatized with boronic acid and that with 3,3'-bithiophene served as the functional and cross-linking monomer, respectively. After electropolymerization, sacrificial silica NPs were dissolved with 1% HF leaving macropores in the MIP film thus enlarging its surface area. For the arabitol template removal, 0.1 M HCl was used. Binding of the arabitol analyte molecules by the imprinted cavities was transduced with piezoelectric microgravimetry at the quartz crystal microbalance. Analytical performance of the chemosensor, including detectability (9 $\mu$M L-arabitol), and sensitivity (-35±12) Hz $mM^{-1}$, was determined under flow injection analysis condition. Moreover, the determined selectivity with respect to common interferences, such as D-arabitol, adonitol, and xylitol, was high.

# Recent advances in biofuel cells

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The lecture will overview the critical advances in biofuel cell technology. Fuel cells that employ biocatalysts are classified as biofuel cells. Among the many different biocatalysts (oxidoreductases, organelles, living cells) enzymes are in general exceptional bioelements, reaching catalytic turnover numbers of $10^7$ $s^{-1}$ [Garrett and Grisham, 2008], *i.e.* close to the diffusion-controlled rates of redox reactions. Thus, at least in theory, enzymes could be used to create the most powerful FCs, compared to microbial or mitochondrial biodevices, and even conventional FCs [Oman, 1999].

Oxidoreductases are natural renewable catalysts, which can be produced at very low costs. The high selectivity of enzymes makes their utilisation in different applications highly advantageous not only commercially, but also scientifically and technologically, by eliminating problems of cross-reactions and catalyst poisoning. This is pivotal in the design of biodevices, since it allows fabrication of membrane-less, single compartment biofuel cells, removing not only voltage losses, but also technical challenges that otherwise transpires. Employing a direct electron trasfer based design allows for significant simplifications and improvements in the construction of biodevices; no soluble compounds need to be added, mediator induced voltage losses can be avoided, and possibly toxic mediator compounds can be excluded; also, these factors simplifies miniaturisation and practical realisation of efficient and accessible bioelectric power sources. Furthermore, many oxidoreductases are active at neutral pH and at room temperature, *i.e.* under the conditions at which an implanted device would operate. These properties enabled the development of extracorporeal or implantable devices for biomedical application, *i.e.* (bio)fuel cells operating in *ex vivo* and *in vivo* situations, respectively [Falk et al., 2012a]. Such applications include monitoring health indicators by a biosensor, or powering of actuators, such as artificial organs or drug delivery systems. The limitations of this widely accepted concept will be discussed in the context of the site of implantation and the alternative use of extracorporeal alternatives, such as electronic patches or "smart" contact lenses [Falk et al., 2012b]. The paper will provide a biomedical outlook on the implantation of biofuel cells as it contrast the *in vivo* operation of such device for demonstration purposes. *In vitro* and *in vivo* studies showed the feasibility of potentially implantable biodevices to work by using different biofuels from human blood, plasma, saliva, and tears [Falk et al., 2012a; Falk et al., 2013]. During the lecture significant attention will be also devoted to proper surface modification procedures to produce nanobiocomposite materials serving as bioanodes and biocathodes of efficient and stable biofuel cells.

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# Probing the regulation mechanism of cytochrome cd1 nitrite reductase - A combined spectroscopic and electrochemical study

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Denitrifying microorganisms use nitrate, instead of oxygen, as an electron acceptor for energy production. Due to the relevance of denitrification in the biological, environmental and biotechnological sciences, the enzymes involved in this pathway have been extensively studied. The cytochrome $cd_1$ nitrite reductases ($cd_1$NiRs) catalyze the one electron reduction of nitrite to nitric oxide. These homodimeric proteins contain in each subunit one heme c, the electron transfer site, and one heme $d_1$, which is exclusive to this class of enzymes and constitutes the active site where the reduction of nitrite takes place. Although reaction mechanisms have been proposed for this enzyme there are still open questions. For example, the rate limiting step of the overall reaction, the repercussion of the redox state of heme c during catalysis, the role of heme $d_1$ in the displacement of NO are controversial topics [1-3].

In this work we studied the *Marinobacter hydrocarbonoclasticus* $cd_1$NiR, using a set of complementary techniques, to evaluate the mechanisms that control the electron transfer (ET) processes prior and during the catalytic reaction. For this purpose we used resonance Raman (RR) based spectroelectrochemical techniques. Surface enhanced RR spectroscopy was performed with $cd_1$NiR immobilized on silver electrodes, coated by alkanethiol based self-assembled monolayers. In this way we could probe the potential dependent ET processes involving hemes c and $d_1$. Upon immobilization, the redox potential of $cd_1$NiR was shifted to more negative potentials when compared to native RR titrations and previous reports.

In parallel studies, the interaction of $cd_1$NiR with its physiological electron donor, cytochrome $c_{552}$, was characterized by electrochemistry and molecular bioinformatics. Cyt $c_{552}$ displays a reversible reaction at carbon electrodes and therefore cyclic voltammetry could be used to learn about the intermolecular ET between the two redox partners. Moreover molecular docking was used to model the complex $cd_1$NiR - cyt $c_{552}$. The results from mediated electrochemistry and docking with putative redox partners were compared with other biological and non-biological electron donors.

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# Piezomicrogravimetric and impedimetric oligonucleotide biosensors using conducting polymers of biotinylated bis(2,2?-bithien-5-yl)methane as recognition units

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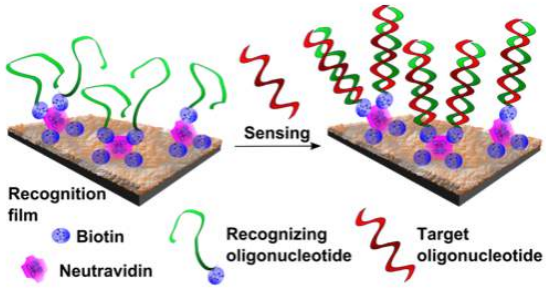


Biosensors for selective determination of oligonucleotide of the 5'-ACT GCT AGA GAT TTT CCA CAT-3' sequence, which was reported earlier as the single-stranded DNA capable of recognizing the HIV-1 virus,[1] were devised and fabricated. Electrochemical impedance spectroscopy (EIS) or piezoelectric microgravimetry (PM) were used for label-free analytical signal transduction. For preparation of the biosensors recognition unit, the bis(2,2'-bithien-5-yl)methane functional monomer was designed and synthesized. Then, this monomer was potentiodynamically polymerized on surface of a glassy carbon electrode (GCE) and of an Au electrode of a quartz crystal resonator (QCR) for the EIS and PM transduction, respectively. Next, neutravidin was irreversibly immobilized by complexing the biotin moieties of the polymer. Finally, recognizing biotinylated oligonucleotide was attached by complexing the surface-immobilized neutravidin. This layer-by-layer assembling of the poly(thiophene-biotin)-neutravidin-(biotin-oligonucleotide) recognition film served to determine the target oligonucleotide via complementary base pairing. The resulting sensors were tested and their analytical parameters determined. The limit of detection (LOD) was 0.5 pM and 50 nM for the EIS and PM transduction, respectively. The sensor response to the target oligonucleotide was linear with respect to logarithm of the oligonucleotide concentration in the wide range of 0.5 pM to 30 $\mu$M and with respect to its concentration in the range of 50 to 600 nM for the EIS and PM transduction, respectively. The biosensors were appreciably selective with respect to the nucleobase mismatched oligonucleotides.

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# Ordered biomaterials in electrochemical sensors

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Due to many applications ranging from the detection of disease-causing and food-contaminating organisms to forensic and environmental research, in the last decades there has been observed an increased interest in electrochemical biosensors, especially the ones containing various forms of DNA. Among the nucleic acid bases found in deoxyribonucleic acids, guanine is one of the purine bases characterized by the smallest value of the oxidation potential and it is the most commonly measured product of DNA oxidation [1-4].

The sensor composite layers**,** consisting of nanomaterials combined with a polymer represent a relatively novel idea of creating organized that show many attractive properties, including improved electrochemical behavior. In this work**,** the glassy carbon (GC) electrode covered by a layer of the polymer [poly(3-octylthiophene-2,5-diyl)] combined with multiwall carbon nanotubes (MWCNTs) was used in the ordered architecture of the matrices holding DNAs. Various methods: differential pulse voltammetry (DPV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) as well as scanning electron microscopy (SEM) were used to characterize the sensor. To study the guanine oxidation without the composite, except GC, another type of the electrode, the reticulated vitreous carbon (RVC) foam electrode, was also used.

The presented data clearly indicate that the guanine oxidation process depends on several factors such as: preparation and the type of the surface, accumulation potential, time adsorption, scan rate, temperature, and the solution pH.

The oxidation signals of other nucleic acid bases and their interactions with typical redox indicator, Methylene Blue were also investigated.

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# Preparation of a single polymer fiber via laboratory centrifuge

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Over the past two decades there has been a big increase in the demand for polymeric nano- and micro-fibers. They are promising candidates for applications including composites, tissue engineering, sensors and drug delivery systems.

The most common process used to produce polymer fibers is electrospinning. Other methods include melt blowing, force-spinning, flash-spinning, phase-separation, bicomponent spinning and use of microfluidic systems. In most of these processes the fibers are collected as nonwoven random fiber mats. The range of the size of these fibers is from several nanometers to tens or hundreds of micrometers. The main disadvantages of these methods are:

i) they do not allow to produce a small amount of the fiber in a single process (i.e. a few centimeters long fiber),
ii) mostly are not easy to control (i.e. electrospinning) or
iii) are still in the state of development (microfluidic systems).

We present a new method of preparing single polymeric fiber made of alginate. The method use a typical, laboratory centrifuge and centrifugal force as a 'driving force' in the process of fiber drawing. The process is fast, simple and allow to control the diameter, length and composition of the fiber. The proposed method can be useful in biomedical research for measuring the releasing of the active substance and everywhere where is the need for producing a small amount of short polymeric fibers.

# Targeted Surfaces for Cell Imaging and Sensing

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The generation and fabrication of nanoscopic structures are of critical technological importance for future implementations in areas such as nanodevices and nanotechnology, bio-sensing, bio-imaging, cancer targeting, and drug delivery. Applications of carbon nanotubes (CNTs) in biological fields have been impeded by the incapability of their visualization using conventional methods. Hence, fluorescence labeling of CNTs with various probes under physiological conditions has become a significant issue for their uses in biological processes. Herein, we describe a facile and additional fluorophore-free approach for cancer cell-imaging and diagnosis by combining multi-walled CNTs with a well-known conjugated polymer, namely poly(*p*-phenylene) (PP). In this approach, PP decorated with poly(ethylene glycol) (PEG) was non-covalently (π-π stacking) linked to acid-treated CNTs (f-CNT). The obtained water self-dispersible, stable and biocompatible f-CNT/PP-*g*-PEG conjugates were then conjugated to estrogen specific antibody (anti-ER) via –COOH functionalities present on the side-walls of CNTs. The resulting conjugates were used as an efficient fluorescent probe for targeted imaging of estrogen receptor overexpressed cancer cells, such as MCF-7. *In vitro* cell culture studies and fluorescence microscopy data show that these conjugates can specifically bind to MCF-7 cells with high efficiency. The represented results imply that CNT-based materials could easily be constructed by this approach and used as an efficient "fluorescent probe" for targeting and imaging, thereby providing many new possibilities for various applications in biomedical sensing and diagnosis.

# Studies of the interactions of tailored oligopeptides and copper ions

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The aim of this work was to investigate the competitive binding of copper(II) ions by various newly synthesized oligopeptides, both in solution and immobilized on a solid support.

Cysteine and cysteamine based peptide derivatives were applied to form monolayers on the surface of gold electrode. The optimization of self-assembly process of chosen oligopeptides involved studies on the influence of several factors (time, temperature, concentration of oligopeptide in solution) on the quality of created monolayers. The impact of cysteine (Cys) and cysteamine (CA) headgroups on the organization of molecules in the monolayer was also examined. Replacing Cys in βAlaAlaHis-Link-Cys and AlaAlaHis-Link-Cys (where Ala – alanine, βAla – beta alanine, His – histidine, Link – 6-aminohexanoic acid) by CA contributed to the improvement in monolayer's order and stability. The solution experiments with short tripeptides (without terminal sulfur amino acid): βAlaAlaHis, AlaβAlaHis, AlaAlaHis were carried out to elucidate the nature of the interactions between peptides and copper ions at different oxidation states. The redox properties of peptide-copper complexes were examined by voltammetry techniques and UV-Vis spectroscopy.

The performed studies indicated that the sequence of the three amino acids is crucial for the redox process of copper ions coordinated by peptide ligand, has influence on the structure of the formed peptide-copper complexes and their equilibrium constants. The obtained redox active peptide-Cu(II) conjugates can be applied as new systems to clarify the mechanism of interactions of copper ions and β-amyloid (Aβ), which is an important peptide associated with Alzheimer's disease.

Acknowledgments

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# Development of an electrochemical sensor for Cytochrome c detection

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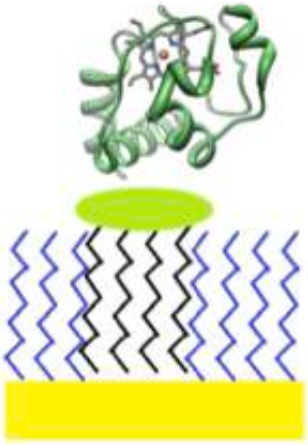
Cytochrome c is an inner mitochondrial membrane (IMM) protein which plays a pivotal role in oxidative phosphorilation. This protein is not detectable in healthy patients blood but it has been demonstrated that during some diseases, which involves the cellular apoptosis, Cytochrome c (*cyt c*) is released[1]. Thus, taking advantage from the redox behavior of the couple Fe(II)/Fe(III) of this Heme protein, *cyt c* is an ideal electrochemical marker of these diseases. Cyt c is released from cellular membrane as a consequence of the treatment of infarction. In particular, currently, the only way to reduce acute myocardial infarction (STEMI) is to treat patients with primary percutaneous coronary intervenction (pPCI).



The abrupt reconstruction of blood causes, in some patients, apoptotic cell death and a bigger myocardial injury, which increases up to 50% the size of infarction[2].

In this scenario there is an urgent need to develop a sensor for quick detection of *cyt c* in very early stages of the disease to evaluate damages and operate with fast bedside therapies.Monitoring *cyt c* concentration can help to control the progression of the infarction.
To mimic the IMM and guarantee the selectivity, we designed a biosensor based on a gold electrode modified with an alkanthiol Self-Assembled Monolayer (SAM), in which we integrate Cardiolipin (CL). This IMM phospholipide is the natural membrane *cyt c* binding site as *cyt c* and CL form a stable complex. In order to develop an electrochemical sensor for *cyt c* detection and to verify the formation of the *cyt c* and CL complex, we performed ciclovoltammetric and spectroelectrochemistry experiments. Further investigations are required to optimize the *cyt c* binding to CL modified surfaces and to lower the sensibility of our sensor.

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# Surface modification for chemical sensing of thin films formed by remote hydrogen microwave plasma CVD using organosilane precursors

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Silicon-based thin-film materials such as silicon oxycarbide or silicon carbonitride owing to their many unique properties: high adhesion and hardness, low friction coefficient, excellent resistance to penetration of highly corrosive chemicals and a very good conformality of coverage, are considered to be particularly useful for the preparation of chemical sensors. The excellent mechanical, tribological, and chemical properties of deposited films significantly improve the performance of coated elements and substrates. In our research we use a remote hydrogen microwave plasma chemical vapor deposition (RP-CVD) technique to form thin films from organosilanes – particularly using tetramethyldisiloxane (TMDSO, $(Me_2SiH)_2O$) as single-source precursor. The technique offers well-controlled deposition conditions free from film damaging effects and produces morphologically homogeneous coatings of the properties well controlled by the substrate temperature (1).

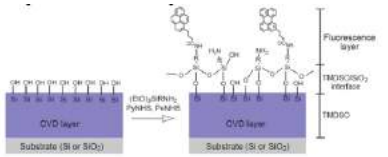


Fig. Schematic illustration of fluorescence TMDSO layers.

Silicon surfaces were further chemically modified with fluorescence molecules as sensors, which were then immobilized at the surface (2). For this purpose, the surface of the organosilicon coating was activated by hydroxyl groups produced by a conventional radio frequency (RF) plasma treatment using $Ar/H_2O$ mixture for plasma generation. The activated TMDSO film substrates were placed into a vapor phase deposition system for the immobilization of the aminosilane molecules (APTES). Then the surface was immersed in a solution of pyrene and perlylene derivatives in $CH_2Cl_2$. Modification of silicon oxycarbide thin film surfaces, following plasma treatment, was examined at various stages using the ellipsometric, contact angle, AFM, FTIR, and fluorescence techniques.

The present work was supported by the National Center for Sciences in a frame of the research project UMO-2012/05/B/ST/00366.

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# Adjustment of the Standard Potential of Solid-Contact Ion-Selective Electrodes. Comparison Between Different Types of Ion-Selective Membranes

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In solid-contact ion-selective electrodes (ISE), where conducting polymers (CP) are used as ion-to-electron transducers between the ion-selective membrane (ISM) and electrical conductor (fig. 1a-b), the analytical signal is formed at the solution | ion-selective membrane (ISM) interface, but the overall potentiometric signal contains contribution from the CP-layer. The potentiometric signal of the CP itself is dictated by its redox state and ionic equilibrium that are influenced both by polymerization conditions and by the composition of the contacting solution [1].

In this work it is shown that the standard potential (E°) of ISEs can be manipulated by adjusting the redox state of the CP by applying current or potential in a conventional three-electrode cell set-up (fig 1c). The applicability of this method to different types of ISMs is studied and the stability, reproducibility and analytical usefulness of the shift of E° is evaluated. Three different membranes are chosen for the study: (i) a general cation sensitive membrane, (ii) a potassium selective membrane and (iii) a potassium selective membrane containing lipophilic additive. Membranes (i) and (iii) are prepared with two different ratios of plasticizer and poly(vinyl chloride) in order to compare effect of resistivity of the membrane to tuning of E°. The conducting polymer used as solid-contact in this study is poly(3,4-ethylene dioxythiophene) doped with poly(sodium 4-styrenesulfonate), i.e. PEDOT(PSS).

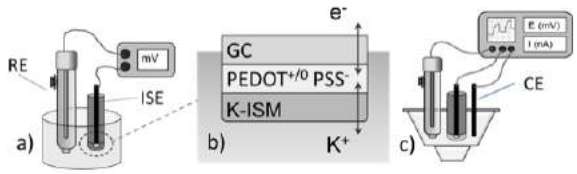


*Fig. 1 Schematic picture of*
*a) potentiometric open circuit measurement with ISE*
*b) ion-to-electron transduction via reduction/oxidation of the conducting polymer PEDOT*
*c) measurement set-up where potential or current through ISE can be controlled while the other one is measured*

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# EIS investigations on modified interfaces for the detection of allergen proteins

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Biosensors have emerged in the recent years as powerful alternatives to current standard Enzyme- Immuno-Linked Assay tests for the detection of allergen proteins. A careful control of biosensor architecture is required, as this represents the driving factor of its overall analytical performance and directly influences the ratio between the specific and non-specific response. Electrochemical Impedance Spectroscopy (EIS) is a label-free analytical technique, extremely sensitive to changes at sensing interfaces that are translated into modifications of the resistance to charge-transfer and the double layer characteristics [1]. By consequence, EIS is very valuable in monitoring the different stages in the construction of a biosensor.

Various approaches for the modification of carbon-based and gold electrodes have been investigated in order to obtain biosensors for the detection of allergens such as lysozyme and gliadin. Specificity of the assays was achieved using antibodies (gliadin) or aptamers (lysozyme). EIS studies allowed to optimize sensor architecture and to minimize non-specific adsorption. The evaluation of non-specific binding by EIS is presented in detail, including approaches such as coating the sensor with self-assembled monolayers of thiols that contain ethyleneglycol groups versus blocking with proteins (e.g Bovine Serum Albumin).

In the recent years, coupling EIS with Surface Plasmon Resonance (SPR) has emerged as the preferred approach of many researchers to obtain a complete image of the phenomena occurring at the sensor surface, since both techniques are label-free and allow real-time monitoring. Therefore advantages but also the challenges and limitations of EIS will be discussed in the context of complementary information provided by other electrochemical techniques and by SPR [2].

Future perspectives in the use of EIS for optimising sensor interfaces for the sensitive detection of allergens will be presented.

Acknowledgements:
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# Study of lysozyme aggregation using glassy carbon and boron-doped diamond nanowire electrodes

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Lysozyme is a 14kDa protein that can form amyloid-type fibrils in vitro and was previously used as a model in aggregation studies. This work presents an approach towards the electrochemical monitoring of lysozyme aggregation at pH 2 and 60º C, based on direct oxidation on glassy carbon and boron-doped diamond nanowire electrodes. Lysozyme contains 3 tyrosine and 6 tryptophan residues, which are electrochemically active. On glassy carbon electrodes, oxidation potentials of tyrosine and tryptophan at pH 2 are very close, 0.820 and 0.855 V respectively vs. Ag/AgCl, 3M KCl, Instead, using boron-doped diamond nanowires, the oxidation of tryptophan and tyrosine occurred at 0.87 and 1.10 V vs. Ag/AgCl respectively.

Despite this remarkable separation in binary mixtures, it was not possible to separate the contributions due to these two aminoacids in lysozyme using the boron-doped diamond nanowires electrodes. Possibly this was due to the complex environment in the protein and to the higher sensitivity of the electrodes to tryptophan as compared to tyrosine.

Glassy carbon [1] and boron-doped diamond nanowires electrodes presented similar analytical performances with respect to the determination of lysozyme by Square Wave Voltammetry, allowing a detection limit of 1 $\mu$g/mL and a linear range up to 30 $\mu$g/mL. Square Wave Voltammetry results were supported by data obtained in electrochemical Impedance Spectroscopy experiments and Thioflavin T fluorescence measurements.

Both types of electrodes studied in this work are appropriate for studying protein fibrillation in acid media.

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Vasilescu A, Gaspar S, Mihai I, Tache A, Litescu SC., *Analyst* **2013**, *138 (12),* 3530 – 3537

# Can bigger do better? Comparison of two architectures of potentiometric sensor arrays used in electronic tongue system

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Electronic tongue is a multisensory system dedicated to qualitative and quantitative analysis of fluid samples with complex matrix. It is composed of a set of cross – selective sensors (a sensor array) and a data analysis system (*Pattern Recognition block*, PARC), which allows one to extract useful information from sensor responses. The aim of such analysis is recognition and classification of samples images. The number of papers describing the application of electronic tongue for the measurement of environmental samples, biotechnological samples, food, body fluids and pharmaceuticals is steadily growing.

The aim of this work was to compare two architectures of sensor arrays: composed of standard ion-selective electrodes (ISEs) and composed of miniaturized ion-selective electrodes. Measurements carried out with a sensor array formed by standard ISE were performed in stationary conditions, whereas miniaturized ISE sensor array was adapted to flow-through measurements.

Electronic tongues based on standard ISEs and miniaturized ISEs were used to asses taste masking effectiveness in pharmaceuticals. Both type of electrodes were used in sensor array to evaluate the "taste" (different chemical images formed with the use of sensor array) of active pharmaceutical ingredient (API) before and after microencapsulation. The spray drying technique was chosen for microencapsulation process of API and pure Eudragit L30D-55 and Eudragit L30D with addition of SLS were used as taste masking coats.

Chemometric analysis of signals was conducted by Principal Components Analysis (PCA) in order to detect microencapsulation effect of API, which influences taste properties of pharmaceuticals. The performed analysis showed preliminary evidence of the possibility of electronic tongue application for the investigation of efficiency encapsulation process of active pharmaceutical ingredients for taste masking purposes.

This work has been supported by National Center for Research and Development within a framework of LIDER programme (Nr LIDER/17/202/L-1/09/NCBiR/2010) and from the resources for science in years 2013 – 2017 as a research project within a framework of "Diamond Grant" programme.

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# Integrating molecularly imprinted polymers with sensors and assays

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Selective sensing of drugs, including drugs of abuse, biomarkers, agricultural chemicals, pollutants, food adulterants, explosives and nerve agents are all proposed uses of molecularly imprinted polymers (MIPs) [1]. What are the challenges involved with integrating MIPs with transducers and in assays and how are they being overcome? This presentation will give examples of MIP sensors [2,3] and MIP-based assays from our work and from other laboratories as to how these challenges are being met, including through the use of nanomaterials [4-6]. The prospects for commercial exploitation will be discussed.

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# Nanoparticles in a Capillary Trap: Dynamic Self-Assembly at Fluid Interfaces

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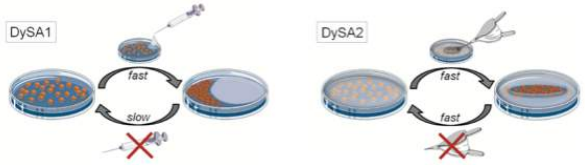
Dynamic self-assembly (DySA) is an emerging scientific concept aimed to construct artificial systems of adaptative behavior. Here, we present a first nanoscopic system that is able to dynamically self-assemble in two dimensions.[1] This system is composed of charged gold nanoparticles, uniformly dispersed at the air-water interface. Creation of the gradient of the surface tension makes the NPs migrate towards the area of higher tension with formation of a dense monolayer. Spatial distribution of the surface tension is controlled by the presence of organic solvent over the fluid interface. The NP structures are present as long as the surface tension gradient is maintained. At equilibrium, when this gradient vanishes, the NPs return to their initial, dispersed state.

The designed DySA system can work in two different modes: either by introducing organic solvent (DySA1) or by removing it from the interface (DySA2). These two systems differ in the way the energy flux needed to sustain the dynamic structures is supplied and dissipated. DySA1 system offers a chemical alternative for the Langmuir-Blodgett technique and, therefore, can be employed for the fabrication of the large-area NP monolayer films which have aroused recently the great practical interest as potential component for novel devices and materials. In turn the fast-responding version of the NP self-assembly, that is DySA2, was successfully applied for creation of self-erasing NP patterns at the gas-liquid interface.

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# Coupling and monitoring chemical fluxes of microstructured enzyme layers

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The talk will explain how different scanning probe techniques can be used to elucidate structural and functional details of multi-enzyme microstructures.[1, 2] Layers of glucose oxidase (GOx) and horseradish peroxidase (HRP) were prepared by layer-by-layer deposition inside microfluidic networks onto glass substrates in order to allow both, site specific deposition and control of the amount of immobilized enzymes.[3] The obtained microstructures were characterized by scanning force microscopy for the topography of the deposited layers. The local enzyme activity was characterized by the substrate-generation/tip-collection mode[4] and the enzyme-mediated feedback[5] mode of the scanning electrochemical microscope (SECM).[6] These measurements provided quantitative information about the immobilized enzyme activity as a basis for adjusting enzyme loading for multi-enzyme structures that realize logical operations based on enzymatic conversions. The information on local HRP activity can also be obtained by optical readout using a fluorgenic substrate Amplex Ultra Red(TM) and reading with a confocal laser scanning microscope with a much higher repetition rate for image acquisition. Using those principles, a layout with HRP and GOx microstructures was realised that showed the functionality of an OR Boolean logic switch.

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# Recent progress in bioelectrocatalytic systems with multidomain enzymes

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The catalytic reaction in multicenter enzymes is accompanied by intra and/or intermolecular electron transfer steps. Electrochemical investigations can provide important information about these enzymes. Importantly, such studies also enable us to develop biomolecular modules for bioanalytics, energy conversion and signal transfer. In bioelectrocatalytic systems the catalytic reaction of redox enzymes is connected with transfer of redox equivalents to electrodes. For effective bioelectrocatalysis it is essential to achieve a fast communication between the protein and the electrode, while the biocatalytic activity is preserved. The main aspects to be considered are therefore the biocatalyst itself, the surface and the matrix for stabilization and charge transfer. Electronic communication can be achieved by a direct heterogeneous electron transfer or by electron transfer mediators. This process is well investigated assemblies of small redox proteins, e.g. cytochrome c. Complex enzymes such as multidomain enzymes can often only be addressed by mobile mediators. Chemical modification of the electrode surface and special surface architectures can however also provide here a way to achieve a direct communication, which is critically dependent on the special orientation of the communicating redox site. In recent developments we benefit from enzyme technology and surface science as well as from the progress made in the fabrication of support materials that serve as the interface between the biomolecules and the electrical circuit including the readout device. We will show examples with 3-D spectroelectrochemical devices with transparent conductive mesoporous electrodes, conductive and semiconductive nanoparticles.

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Frasca, S., Rojas, O., Salewski, J., Neumann, B., Stiba, K., Weidinger, I. M., Tiersch, B., Leimkühler, S., Koetz, J., Wollenberger, U. Human sulfite oxidase electrochemistry on gold nanoparticles modified electrode Bioelectrochemistry, 87 (2012) 33-41

# Nanoparticles ? golden hope for Microbial Fuel Cells

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Microbial fuel cells (MFCs) represent a highly interesting and innovative part of science. A lot of research has been carried out to elucidate the potential of MFCs for production of electricity and waste remediation. One of the most challenging parts of electricity production by MFCs is the limited conductivity through the biofilm on the anode and, recently, research attention has focused on the use of different nanoparticles to enhance electron transfer from the microbe to the anode.

In this study, we aim to use amphipol-encapsulated $CuInS_2$/ZnS (CIS-QDs) quantum dots (1), encapsulated in to test whether nanoparticles can be incorporated into biofilms. Results will be used to design a strategy to incorporate gold nanowires (GNWs) into MFCs. The toxicity of CIS-QD to MFC model bacteria – *Shewanella oneidensis* MR-1 – was evaluated and showed no statistically significant level while at the same time the amphipol on its own showed the ability to promote bacterial growth. The interaction of CIS-QDs with bacterial cells was studied using fluorescence microscopy.

In conclusion, CIS-QDs as nontoxic nanoparticles, showed the potential for visualization and doping bacterial biofilms in MFCs, however GNWs will need further evaluation in terms of toxicity and possible interactions with bacteria.

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# Third Generation ATP Sensor with Enzymatic Analyte Recycling

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Adenosine-5`-triphosphate (ATP) is the main intracellular energy source. It is involved in different signaling processes released into the extracellular surrounding after various mechanical and chemical stimuli. The space-resolved measurement of ATP in the lower $\mu$M range is still a challenge. Amperometric biosensors based on immobilized multienzyme systems have been developed since ATP cannot be directly indicated. The most prominent sensor uses glucose oxidase (GOx) and hexokinase (HK) and evaluates the decrease in peroxide production in the presence of ATP [1,2]. Under optimal conditions the sensitivity of ATP approaches that of glucose because one glucose molecule can be converted for each ATP. Signal amplification by enzymatic recycling of ATP back to ATP has been applied in order to increase the sensitivity for ATP [3].

Here for the first time the signal generation by the direct electron transfer (DET) of a glucose-converting enzyme - a mutant of cellobiose dehydrogenase (CDH) - has been coupled with the HK catalyzed competition for glucose in presence of ATP. To enhance the signal output for ATP, pyruvate kinase (PK) was coimmobilized to recycle ADP by the phosphoenolpyruvate (PEP) driven reaction.

The three enzymes have been successfully immobilized by adsorption to the polydiallyldimethylammonium chloride (PolyDADMAC) modified graphite electrode. After optimisation of the amount and the ratio of the 3 enzymes the catalytic current for glucose was comparable to that of the CDH sensor. Obviously the negatively charged CDH is not markedly displaced by the presence of the two other enzymes. Both CDH and HK will be bound to the positively charged surface by electrostatic forces. On the other hand, the positively charged PK may be trapped by the interaction with the oppositely charged proteins as the signal amplification on addition of PEP indicates. The simple adsorption of the three enzymes on the (PolyDADMAC) modified surface is surprisingly effective as it is indicated by only 30 % signal decrease within 5 h incubation in the measuring buffer. The three enzyme electrode shows a linear measuring range for glucose from up to 1 mM. No measurable signal was obtained below 100 $\mu$M ATP without enzymatic signal amplification. Addition of PEP brings about a signal amplification by recycling of ATP which results in a measuring range between 2 $\mu$M and 20 $\mu$M ATP.

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# Bioelectrochemistry and catalytic behaviour of recombinant human sulfite oxidase at nanoparticle modified electrodes

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The *human* sulfite oxidase (*h*SO) is a molybdoenzymes, which catalyzes the oxidation of sulfite to sulfate. This is the terminal step in the degradation of sulfur-containing amino acids and thus of physiological importance. Direct protein electrochemistry of surface immobilized molecules is a powerful tool to investigate the catalytic properties of redox enzyme. Modification of the electrode surface is a crucial step to get efficient interfacial reaction of the enzyme. The efficiency of electron transfer between enzymes and electrodes in bioelectrocatalytic devices can be largely improved when nanostructures are implemented for fabrication. Previously we demonstrated that bioelectrocatalysis with (*h*SO) is enhanced when it was coassembled on a gold electrode with polyelectrolyte capped gold nanoparticles compared to a polyelectrolyte monolayer [1]. Here we will present further improvement of the reaction and a more detailed study about the behavior of *h*SO on the surface and the role of conductivity of the nanoparticles. For this purpose, conductive, non-conductive and semi-conductive nanoparticles were employed. Furthermore the method of nanoparticle binding to the electrode was improved. Cyclic voltammetry was used to probe the direct electron transfer and bioelectrocatalysis of *h*SO on different NPs /SAM layer. The modi?ed electrodes, at different stages of its construction and modified with three different nanoparticles were characterized using Electrochemical Impedance Spectroscopy (EIS) techniques. For example coupling the nanoparticles onto a short SAM layer resulted in a higher electron transfer rate of enzyme and steady state catalytic current. The voltammogram for the bound enzyme shows a clear noncatalytic reversible redox process at the potential of the heme center. Substrate addition results in large catalytic oxidation currents. The catalytic reaction involves intramolecular and heterogeneous electron transfer steps. Variations of the solution conditions were made to influence the single reaction steps. Detailed electrochemical studies show that domain mobility is kept for fast combined intramolecular and heterogeneous electron transfer during sulfite oxidase bioelectrocatalysis, which is also consistent with a model derived for the enzyme in solution studied by using flash photolysis[2] and molecular dynamic simulations from SERR spectroelectrochemistry of *h*SO on monolayer modified electrodes [3].

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# Enhanced photocurrent generation by immobilizing photosystem 1 within a crosslinked Os-complex modified redox hydrogel on a L-cysteine film modified electrode

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Photosystem I (PSI), a protein complex that drives photosynthesis in higher plants (monomers) and cyanobacteria (trimers), represents an efficient converter for the energy of visible light into chemical energy. It attracts growing interest for designing novel bioelectrochemical devices due to its remarkable photocatalytic functionality and close to perfect quantum yield of almost unity. In this work, PS1 was immobilized within a specifically designed redox hydrogel on top of a L-cysteine monolayer on a gold electrode surface. An enhanced catalytic photocurrent upon illumination provides the basis for photobioelectrochemical devices to be integrated in photochemical cells.

Specifically, we have used a crosslinked Osmium-complex modified polymer (P016-P184) which acts as immobilization matrix while simultaneously functioning as electron transfer mediator that wires PS1 with the electrode. A L-cysteine film was electrochemically deposited on the gold electrode surface providing $-NH_2$ groups at the interface to covalently bind the epoxy-group containing redox polymer integrating PSI to the electrode surface. The increased photocurrent of film modified electrodes indicates that the content of PS1 integrated within the crosslinked redox polymer is high demonstrating the productive electron-transfer connection between PS1, the redox hydrogel and the gold electrode.

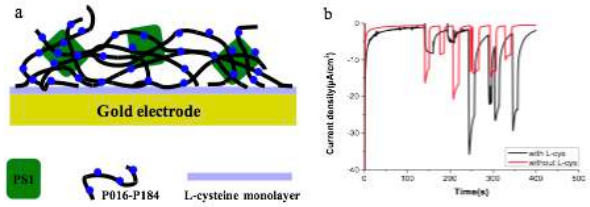


*Fig. 1(a) Schematic representation of PS1 integrated within a crosslinked polymer on an L-cysteine modified Au surface. (b) Comparison of current responses of L-cysteine modified gold electrode (black) and bare gold electrode (red) modified with crosslinked polymer and PS1 upon illumination with white light at different power. The supporting electrolyte is air-satured without bubbling $O_2$, containing 3 mM methylviologen as electron acceptor. The applied potential was -0.05 V vs. Ag/AgCl*

# Truly self-powered sensor for ascorbic acid

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Biofuel cells (BFCs) are expected to be future micropower sources (1). Recently we obtained a very efficient air-breathing biocathode for dioxygen reduction which can be used in BFCs (2). It was composed of single-walled carbon nanotubes (CNTs) functionalized with 1-pyrenesulfonic acid (3) co-immobilised with the enzyme bilirubin oxidase in a silicate matrix. Besides, by simple electrode modification with carbon nanomaterials we obtained anodes for ascorbic acid (AA) oxidation. First example of the anode comprised a forest of vertically aligned CNTs (4), and the second anode contained carbon nanoparticles (CNPs). Both of the anodes were used for constructing $AA/O_2$ BFCs. Due to the fact that the power output of these BFCs was dependent on the AA concentration, they are the examples of self-powered sensors (5). The BFC containing the CNP-anode was connected to an electrochromic display comprising Prussian blue (PB). The PB was reduced after connecting the display to the anode. As a result a change of the display color, with a speed depending on the AA concentration, was observed. The reversed change of the color was observed when the display was connected to the biocathode. Thus a truly self-powered and reusable sensor for ascorbic acid was obtained. To the best our knowledge our sensor was the first one presented so far which gave quantitative information about the analyte concentration. We tested it in the range from 1 – 4 mM AA and used for measuring the AA-concentration in a real sample of orange juice.

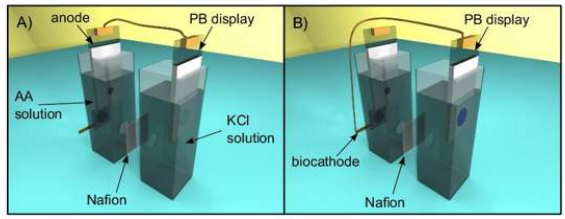


Figure 1 A schematic illustration of the self-powered sensor. In A) the configuration used for AA detection and in B) the configuration for regeneration of the PB-display.

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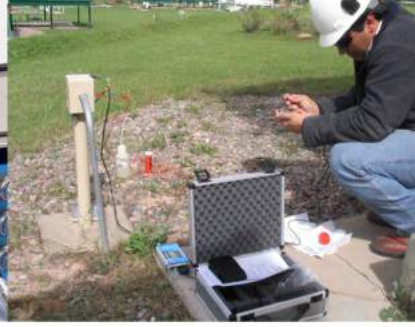
# Index





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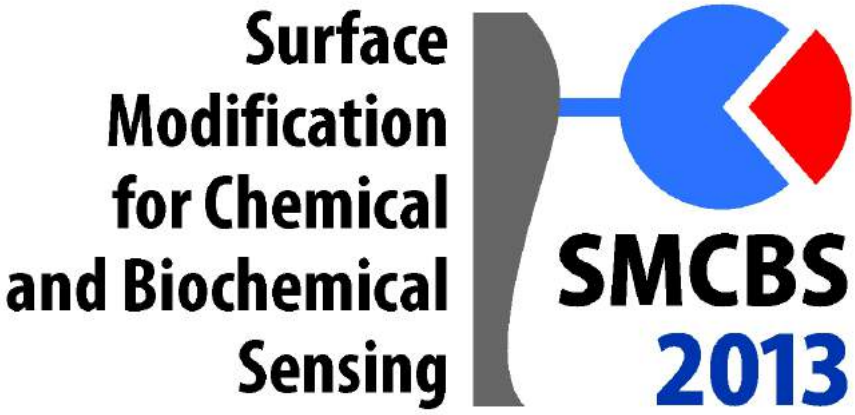


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