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SMCBS 2019

The 9th International Workshop on Surface Modification for Chemical and Biochemical Sensing

Programme & Book of Abstracts

Żelechów (near Warsaw), Poland
8 - 12 November 2019

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The International Society of Electrochemistry
Rue de Sébeillon 9b, CH-1004
Lausanne
Switzerland
Fax: +41 (0)21 648 39

info@ise-online.org
www.ise-online.org

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www.bioelectrochemical-soc.org

LAMBDA SYSTEM
Kreft Barszczewski Spółka Jawna
Kickiego 4a, 50
04-369 Warszawa, Poland

office@lambdasystem.pl
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Spectro-Lab
Warszawska 100/102
05-092 Łomianki, Poland

tel. +48 22 675 25 67
fax. +48 22 811 98 18
info@spectro-lab.pl
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Linegal Chemicals Sp. z o.o.
Kasprzaka 44/52
01-224 Warszawa, Poland

tel. +48 22 631 72 81
info@linegal.pl
www.linegal.pl

Palmsens BV
Randhoeve 221
3995 GA Houten

tel. +31 (0)30 2459211
info@palmsens.com
www.palmsens.com

Polskie Towarzystwo Chemiczne
Freta 16
00-227 Warszawa, Poland

tel. +48 22 831 13 04
biuro@ptchem.pl
www.ptchem.pl

Milo Solutions
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Preface

With a great pleasure and honor we present you the Program and Abstracts of the 9th International Workshop on Surface Modification for Chemical and Biochemical Sensing, SMCBS'2019. The Workshop is organized by the Institute of Physical Chemistry, Polish Academy of Science, Warsaw (Poland) together with the Faculty of Mathematics and Natural Sciences. School of Sciences, Cardinal Stefan Wyszynski University in Warsaw (Poland).

By continuing tradition of previous workshops of the SMCBS series, organized in Białowieża (2003), Kazimierz Dolny (2005), Włodowice (2007), Przegorzały near Cracow (2009), Łochów (2011 & 2013), Pułtusk (2015), and Żelechów (2017), the present workshop hosts all the participants in a single location to give them a unique opportunity to get acquainted, to meet for ad hock discussions, and exchange ideas that might lead to new research concepts and, even more importantly, to launch new collaborations.

In the spirit of previous workshops of the SMCBS series, we are especially happy to welcome many contributions of young scientists who present their results as short oral communications or posters. We are thankful to top specialists in their fields for sharing their latest break-through results presented as keynote lectures. Moreover, we are pleased that half a dozen of scientists of international renown have accepted our invitation to deliver tutorial lectures that can be considered as inspirations for further discussions.

Similarly as formerly, the present interdisciplinary Workshop involves the science of both chemical and non-chemical modification of solid surfaces. Several research works aim at improvement of recognition ability of the resulting chemosensors with respect to target analytes. Main themes of the Workshop include different aspects of surface chemistry, mostly related to chemo- and biosensing in solutions or gases, not being limited to:

- chemo- and biosensing
- chemical and biochemical surface modification
- polymer film coating
- inorganic, organic, and biomaterials for catalysis as well as for electric energy generation and storage
- charge transport in surface films
- novel techniques and instrumentation for surfaces examination
- signal transduction and processing, detection techniques and protocols, system miniaturization and nanotechnology use.

Progress in modern sophisticated chemo- and biosensing requires broad collaboration of specialists not only from the fields of chemistry and biology but also from physics, materials science, electronics, and other. Although, predominately, the SMCBS workshops involve electrochemical aspects of sensing, we hope that the broad spectrum of participants can enjoy the interdisciplinary meetings that give rise to new important sensing ideas.

The Organizing and Program Committee cordially thanks all those who helped making the 9th SMCBS'2019 Workshop a great event. We are particularly thankful to contributing Authors, to the sessions chairing persons, and the members of the International Scientific Advisory Board for their outstanding job done in preparing and evaluating the scientific profile of this event.

On behalf of the Organizing and Program Committee we welcome all the participants wishing them to have a splendid time at the Workshop, both scientifically and socially.

Włodzimierz Kutner
Warsaw, October 2019

Organizers

The Workshop is organized by the Institute of Physical Chemistry of the Polish Academy of Sciences jointly with the Cardinal Stefan Wyszyński University in Warsaw.

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SMCBS'2019

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Institute of Physical Chemistry, Polish Academy of Sciences
jointly with the
Cardinal Stefan Wyszyński University in Warsaw

Żelechów, Poland
November 8-12, 2019

SMCBS'2019 Programme

Friday, November 8

09:00-16:00		**Registration at IPC PAS**
11:45-15:30		**Lunch at IPC PAS**
13:30 / 16:00		**1st / 2nd bus departure to Żelechów**
16:00-19:00		**Setting up posters in the Żelechów hotel**
19:00-20:00		**Dinner**
20:00-21:20		**Evening session** Chairs: F. Marken / Y. Efremenko
20:00-20:40	T01	**Róbert E. Gyurcsányi** Design of SPR Imaging Chips for Multiplexed Affinity Assays
20:40-21:00	K01	**Nicolas Plumeré** Thin Films for Protection of O_2-Sensitive Electrocatalysts
21:00-21:20	K02	**Andreas Lesch** Inkjet Printing of Nanostructured Electrodes for Biosensing

Saturday, November 9

08:00-09:00		**Breakfast**
09:00-10:35		**Morning session 1** Chairs: A. Lesch / E. Suprun
09:00-09:40	T02	**Julea Butt** All Will Be Revealed: Mapping Protein Redox Activity with Protein Film Voltammetry
09:40-10:00	K03	**Lars J.C. Jeuken** Multilayered Lipid Membrane Stacks for Biocatalysis Using Membrane Enzymes
10:00-10:20	K04	**Elisabeth Lojou** Enzymatic O_2 Reduction on Gold Surfaces: Probing Functional Enzyme Immobilization by Coupling Electrochemistry to SPR, Elllipsometry and PMIRRAS
10:20-10:35	SC01	**Ievgen Mazurenko** Orientation-dependent Direct Electrochemistry of Laccase from *Thermus Thermophilus* Reveals Cuprous Oxidase Activity

10:35-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: N. Plumere / I. Mazurenko
11:00-11:20	K05	**Fred Lisdat** Cytochrome C as Valuable Building Block in Multilayered Architectures of Biocatalysts on Electrodes
11:20-11:40	K06	**Johan Bobacka** Ion Sensors with Coulometric Transduction – Limitations and Possibilities
11:40-12:00	K07	**Frédéric Kanoufi** Probing the Interaction of Single Nanoparticle with Interfaces by in Situ Optical Microscopies
12:00-12:20	K08	**Patrizia Romana Mussini** Enantiodiscrimination at Electrochemical Interphases through Implementation of Inherently Chiral Selectors: New Insights and Perspectives
12:20-12:35	SC02	**Vanousheh Rahemi** Hydrogen Peroxide-less Horseradish Peroxidase Based Biosensor for the Detection of Phenols
12:35-12:50	SC03	**Julian Szczesny** Polymer Modified Gas Diffusion Electrodes Containing Hydrogenases or Their Artificial Mimics as Active H_2 Oxidation Catalysts
13:00-14:30		**Lunch**
14:30-16:30		**Afternoon session 1** Chairs: F. Lisdat / J. Szczęsny
14:30-14:50	K09	**Paul A. Millner** Targeted Nanoparticles for Diagnostic and Theranostic Applications
14:50-15:10	K10	**Karolien De Wael** Innovative (Laser Induced) Electrochemical Sensing Strategies
15:10-15:30	K11	**Barbara Jachimska** Development of Dendrimer Based Drug Delivery System
15:30-15:50	K12	**Camelia Bala** Surface Modification for Label-free Sensing
15:50-16:10	K13	**Magdalena Gebala** Dissecting Nucleic Acids Electrostatics - at the Interface of Theory and Experiments
16:10-16:30	K14	**Katarzyna Szot-Karpińska** Label-free Biosensing Platforms based on Bacteriophage Particles for Detection of Diseases Markers
16:30-17:00		**Coffee break**

17:00-18:35		**Afternoon session 2** Chairs: L. Jeuken / E. Lojou
17:00-17:20	K15	**Pawel Krysinski** Surface Properties-dependent Photoelectrochemical Behavior of CdS Nanoparticles
17:20-17:40	K16	**Felipe Conzuelo** Unraveling Photoelectrochemical Processes at Photosystem-based Bioelectrodes by Means of Scanning Photoelectrochemical Microscopy
17:40-18:00	K17	**Alain Walcarius** Electroanalysis with Oriented Nanoporous Silica Thin Films
18:00-18:20	K18	**Zbigniew Stojek** Modification of Electrode Surface with Multifunctional Nano- and Micro-Layers of Materials Sensitive to Environmental Parameters
18:20-18:35	SC04	**Piotr Warszyński** Formation of Casein and Polypeptide in Multilayer Films and Binding of Calcium
19:00-20:00		**Dinner**
20:00-22:00		**Poster session**

Sunday, November 10

08:00-09:00		**Breakfast**
09:00-10:35		**Morning session 1** Chairs: P. Krysiński / J. Bobacka
09:00-09:40	T03	**Francis D'Souza** Interfacial Electron Transfer of Multimolecular Assemblies on Metal Oxide Semiconductors
09:40-10:00	K19	**Frank Marken** Polymers of Intrinsic Microporosity (PIMs) in Electrochemistry
10:00-10:20	K20	**Stéphane Arbault** Using Cold Plasmas to Improve Electrochemical Sensors and vice versa
10:12-10:35	SC05	**Krzysztof R. Noworyta** Oxidation and Coupling of the Selected Carbazole Derivatives – Why It Does Not Always Lead to Polymer Formation
10:35-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: K. Noworyta / A. Yarman

11:00- 11:20	K21	**Karsten Haupt** Molecularly Imprinted Polymer Nanoparticles as Synthetic Antibody Mimics for the Detection and Modulation of Cellular Function and Immunotherapy
11:20- 11:40	K22	**Frieder W. Scheller** Electrosynthesized MIPs for Peptides and Proteins
11:40- 12:00	K23	**Peter A. Lieberzeit** From Self-organized Monolayers to Surface Molecular Imprints: Assay Formats Extending Beyond the Obvious
12:00- 12:20	K24	**Cédric Ayela** Combining Molecularly Imprinted Polymers (MIPs) with Micro (Opto) Electro Mechanical Systems (M(O)EMS) for Improved Chemical Sensing
12:20- 12:35	SC06	**Yasuo Yoshimi** Application of Swelling Phenomena of Molecularly Imprinted Polymers by Specific Interaction with the Target Molecule for Sensing Technology
12:35- 12:50	SC07	**Cecilia Cristea** Biomimetic Approaches over Direct Detection of Antibiotics from Real Samples
13:00-14:30		**Group Photo & Lunch**
14:30- 16:20		**Afternoon session 1** Chairs: R. Gyurcsanyi / F. Conzuelo
14:30- 14:50	K25	**Pawel J. Kulesza** Development of Highly Specific Interfaces for Photoelectrochemical and Electrocatalytic Reduction of Carbon Dioxide
14:50- 15:10	K26	**Ambra Giannetti** A Fluorescence-based POCT Device for Immunosuppressant-drug Monitoring in Transplanted Patients
15:10- 15:30	K27	**Joanna Niedziółka-Jönsson** Long-Period Fiber Gratings for Sensing and Biosensing
15:30- 15:50	K28	**Sebastian Maćkowski** Sensing with Plasmonically Active Metallic Nanostructures
15:50- 16:05	SC08	**Wolfgang Fritzsche** Localized Surface Plasmon Resonance (LSPR) on Metal Nanoparticles for Bioanalytical Applications
16:05- 16:20	SC09	**Simone Berneschi** Optical Microbubble Resonators as Emerging Tools for Environmental Sensing: the “Safe Water” Project
16:30-19:00		**Social program**
19:00-22:00		**Dinner/Banquette**

Monday, November 11

08:00-09:00		**Breakfast**
09:00-10:35		**Morning session 1** Chairs: A. Giannetti / Y. Yoshimi
09:00-09:40	T04	**Gary J. Blanchard** Interfacial Free Charge Density Gradients in Room Temperature Ionic Liquids and Their Potential Applications
09:40-10:00	K29	**Ilaria Palchetti** Novel Materials for Electrochemical Biosensing of Nucleic Acids
10:00-10:20	K30	**Gerd-Uwe Flechsig** Detection of DNA Cross-linking with Cisplatin by Redox-switching of DNA Viscoelasticity Using EQCM
10:20-10:35	SC10	**Elena V. Suprun** Electrocatalytic Sensing of Protein and DNA Molecules on Prussian Blue Modified Electrodes
10:35-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: K. Haupt / S. Arbault
11:00-11:20	K31	**Marcin Opałło** Scanning Electrochemical Microscopy Detection of the Hydrogen Peroxide and Hydrogen Generated at Liquid-Liquid Interface
11:20-11:40	K32	**Wojciech Nogala** Nanoscale Mapping of Chemical and Biochemical Activity at Modified Surfaces
11:40-12:00	K33	**Stefania Rapino** Functional Imaging of Cellular Processes Using Scanning Electrochemical Microscopy
12:00-12:20	K34	**Vitali Syritski** Molecularly Imprinted Polymers Interfaced with Label-free Transducers: towards Development of Chemosensors for Medical Diagnostics and Environmental Monitoring
12:20-12:35	SC11	**Aysu Yarman** Epitope-MIP for Engineered Enzymes
12:35-12:50	SC12	**Yulia Efremenko** Electrical Control of the Receptor Affinity
13:00-14:30		**Lunch**
14:30-16:25		**Afternoon session 1** Chairs: P. Lieberzeit / C. Cristea
14:30-14:50	K35	**Alexander Kuhn** Electronic Diversion of Enzymes for Carrying Out Unconventional Tasks

14:50- 15:10	K36	**Mathieu Etienne** Bacterial Biocomposite Materials: a Tool for Optimizing and Studying Extracellular Electron Transfer Reactions
15:10- 15:30	K37	**Tautgirdas Ruzgas** Wireless, Battery-less Biosensor Tags Based on Direct Electron Transfer Reactions
15:30- 15:50	K38	**Ulla Wollenberger** Bioelectrocatalysis and Bioanalytical Applications of Molybdoenzymes
15:50- 16:10	K39	**Sławomir Sęk** Electron Transport in Nanoscale Junctions with Helicomimetic Foldamers
16:10- 16:25	SC13	**Łukasz Półtorak** Simple Methods for the Electrified Liquid – Liquid Interface Downscaling. From Design to Sensing Applications
16:25-17:00		**Coffee break**
17:00- 18:25		**Afternoon session 2** Chairs: W. Nogala / S. Rapino
17:00- 17:20	K40	**Insung S. Choi** Single-cell Nanoencapsulation
17:20- 17:40	K41	**Jenny Emnéus** 2D and 3D Lab-on-a-Chip Systems for Life Science Applications
17:40- 17:55	SC14	**Maciej Cieplak** Protein imprinting. Better control over deposited polymer structure for better sensor performance.
17:55- 18:10	SC15	**Aleksandra Jaworska** Towards SERS-based Detection of DNA Mutations
18:10- 18:25	SC16	**Lidia J. Opuchlik** About Gold Nanotriangles and Their Applications
19:00-20:00		**Dinner**
21:00-		**Disco**

Tuesday, November 12

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: A. Kuhn / Ł. Półtorak
09:00-09:40	T05	**Sergey Shleev** Non-invasive Electrochemical (Bio)sensors Operating in Human Physiological Fluids
09:40-10:00	K42	**Hanna Radecka** Ultrasensitive Electrochemical Sensors for Exploring of Anion Recognition Processes at Aqueous/Solid Interface
10:00-10:15	SC17	**Nabila Yasmeen** Electropolymerized Molecularly Imprinted Polymer towards Chemosensing of an Autism Biomarker
10:15-10:30	SC18	**Luís C. Almeida** Electrosynthesized Poly(catecholamine) Films Modified with Ethanolamine for Immunosensing
10:30-11:00		**Coffee break**
11:00-12:00		**Morning session 2** Chairs: S. Shleev / K. Szot-Karpińska
11:00-11:20	K43	**Lo Gorton** Connecting Biological Membranes and Bacterial Cells to Electrodes through Redox Polymers
11:20-11:35	SC19	**Kamila Łępicka** The poly[NBI-(DTP)2] as an electrode material for the inherently asymmetric supercapacitor
11:35-11:50		Closing
12:00-13:00		**Lunch**
13:30-		**Departures**

T01. **Design of SPR Imaging Chips for Multiplexed Affinity Assays**

László Simon, Zsófia Bognár, Róbert E. Gyurcsányi

BME "Lendület" Chemical Nanosensors Research Group, Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szent Gellért tér 4, H-1111, Budapest, Hungary
robertgy@mail.bme.hu

In terms of affinity assays surface plasmon resonance imaging (SPRi) offers high throughput, label-free and real-time monitoring of the binding kinetics. However, it offers also in a broader sense an extremely sophisticated platform for understanding the immobilization of synthetic and natural receptors on gold that can provide the basis of rational chemical modification of nanoconfinements. Such modifications require extreme control over the surface concentration and distribution of immobilized receptors that we will show that is feasible by appropriate methodology. Indeed, the difficulties we encountered in the chemical modification of gold nanopores with nucleic acids probes, especially peptide nucleic acids (PNA),[1] were solved after gaining a deeper insight on the relevant immobilization and binding processes through a surface plasmon resonance imaging (SPRi) study.[2] Within this study we developed methods for quantitative determination of the surface concentration of DNA/ PNA probes and their reliable self-regulation within a single-step process.[3]

The general requirement for the efficient use of SPRi is the localized immobilization of the studied receptors while strictly controlling (determining) their surface concentration. The localized immobilization is done by an off-line microspotting (or microelectrospotting)[4] procedure which hinders the direct determination of the surface concentration of the immobilized receptors. We are going to show how these can be determined for PNA and DNA and aptamer probes. Most importantly we found that for all DNA probes the small molecular weight ruthenium(III) hexamine complex (RuHex) introduced earlier for electrochemical quantitation of DNA coverage on gold electrodes can be used also in SPRi to assess the surface density of DNA probes in DNA microarrays.[5] A single injection of RuHex solution allows the simultaneous visualization and quantification of the surface density of DNA probes (ranging in this study from 4×10^{11} to 1.7×10^{13} molecules cm^{-2}) on all spots of a DNA microarray made by microspotting thiol labeled short DNA probes both in prehybridized and single-stranded form on a gold SPRi chip. The excellent controll over the surface concentration of nucleic acid probes could be used for increased efficiency hybridization and protein assays.

Acknowledgements:
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K01. **Thin Films for Protection of O_2-Sensitive Electrocatalysts**

Huaiguang Li,[a] Darren Buesen,[a] Sébastien Dementin,[b] Christophe Léger,[b] Vincent Fourmond,[b] Nicolas Plumeré[a]

[a] *Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsstr. 150, D-44780 Bochum, Germany.*
[b] *Laboratoire de Bioénergétique et Ingénierie des Protéines. CNRS, Aix Marseille Université, Marseille, France*
nicolas.plumere@rub.de

Energy conversion schemes involving dihydrogen hold great potential for meeting sustainable energy needs, but widespread implementation cannot proceed without solutions that mitigate the cost of rare metal catalysts and the intrinsic O_2-instability of bio-inspired replacements. Recently, thick films (>100 µm) of redox polymers were shown to prevent O_2 catalyst damage,[1,2] but also resulted in unnecessary catalyst load and mass transport limitations.[3] Here, we apply novel homogeneous thin films down to 3 µm[4] that provide O_2-immunity while achieving highly efficient catalyst utilization. Our empirical data is explained by modeling demonstrating that resistance to O_2 inactivation can be obtained for non-limiting periods of time when the optimal thickness for catalyst utilization and current generation is achieved even when using highly fragile catalysts such as the enzyme hydrogenase. We show that different protection mechanisms operate depending on matrix dimensions and intrinsic catalyst properties, and can be integrated together synergistically to achieve large and stable H_2 oxidation currents in the presence of O_2, potentially enabling a plethora of practical applications for bio-inspired catalysts in harsh oxidative conditions.

Acknowledgements:
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K02. **Inkjet Printing of Nanostructured Electrodes for Biosensing**

Andreas Lesch,[a] Milica Jović,[b] Victor Costa Bassetto,[b] Yingdi Zhu,[b] Horst Pick,[c] Bhawna Nagar,[b] Domenica Tonelli,[a] Hubert H. Girault[b]

[a] *Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy.*
[b] *Laboratory of Physical and Analytical Electrochemistry, Ecole Polytechnique Fédérale de Lausanne (EPFL) Valais Wallis, Sion, Switzerland.*
[c] *Institute of Chemical Sciences and Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland.*
andreas.lesch@unibo.it

Inkjet printing (IJP) gains continuously in importance in the field of sensor development. As a digital material deposition technique, IJP is suitable to print with micrometer resolution thin layers of a broad range of material containing inks. Compared to screen printing, major advantages include contact-less and mask-less fabrication with up-scalability from prototype to industrial production level. Furthermore, only few hundred microliters of ink, thus extremely low amounts of electrode materials, are required in drop-on-demand, piezoelectric inkjet printers to fabricate hundreds of sensors in reasonable time, making IJP very attractive for developing, prototyping and manufacturing. Major bottlenecks are the ink formulation to achieve stable jetting of picoliter droplets, high dispersibility of nanoparticles to avoid nozzle clogging and well-adhered, defect-free films on substrate surfaces of interest.

Herein, we shall demonstrate the successful development and application of inkjet printed amperometric electrodes based on carbon nanotubes (CNT) and graphene nanosheets. Flexible and transparent CNT electrodes have been used on a large-scale as voltammetric sensors to measure erythrocyte concentrates in blood transfusion medicine[1] and as electrochemiluminescence platforms for cancer diagnostics.[2] In combination with antibodies on magnetic beads, inkjet-printed microtiter plate electrodes have been used to detect rapidly bacterial species and to identify the antimicrobial resistance of such in infected blood samples in a point-of-care (POC) electrochemical reader.[3]

We shall further demonstrate how inkjet printing can be applied for the synthesis of nanostructured electrode coatings by combining IJP of molecules and salts with light processing. For instance, we have combined IJP with UV photopolymerization to coat CNT electrodes with nanometer-thin polyacrylamide hydrogels that were for instance applied for the detection of molecular bacteria markers in wound fluids.[4] Finally, metal and mixed metal nanoparticles can be accurately and rapidly synthesized *in situ* directly on the electrodes by combining inkjet printing of metal precursor salts with pulsed light irradiation. In this process, named Print-Light-Synthesis, thin liquid films containing precursor salts are printed and immediately exposed to microsecond light flashes from a Xe flash lamp. The result is a light-induced reduction of the precursors under ambient conditions without the need of using nanoparticle capping agents or surfactants. All side products of the reactions are gaseous. Examples will include the fabrication of Pt-nanostructured ITO-coated glass slides[5] and Ni/CNT as well as $Ni_xFe_{(1-x)}$/CNT electrodes.[6]

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Saturday, November 9

08:00-09:00		**Breakfast**
09:00-10:35		**Morning session 1** Chairs: A. Lesch / E. Suprun
09:00-09:40	T02	**Julea Butt** All Will Be Revealed: Mapping Protein Redox Activity with Protein Film Voltammetry
09:40-10:00	K03	**Lars J.C. Jeuken** Multilayered Lipid Membrane Stacks for Biocatalysis Using Membrane Enzymes
10:00-10:20	K04	**Elisabeth Lojou** Enzymatic O_2 Reduction on Gold Surfaces: Probing Functional Enzyme Immobilization by Coupling Electrochemistry to SPR, Elllipsometry and PMIRRAS
10:20-10:35	SC01	**Ievgen Mazurenko** Orientation-dependent Direct Electrochemistry of Laccase from *Thermus Thermophilus* Reveals Cuprous Oxidase Activity
10:35-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: N. Plumere / I. Mazurenko
11:00-11:20	K05	**Fred Lisdat** Cytochrome C as Valuable Building Block in Multilayered Architectures of Biocatalysts on Electrodes
11:20-11:40	K06	**Johan Bobacka** Ion Sensors with Coulometric Transduction – Limitations and Possibilities
11:40-12:00	K07	**Frédéric Kanoufi** Probing the Interaction of Single Nanoparticle with Interfaces by in Situ Optical Microscopies
12:00-12:20	K08	**Patrizia Romana Mussini** Enantiodiscrimination at Electrochemical Interphases through Implementation of Inherently Chiral Selectors: New Insights and Perspectives
12:20-12:35	SC02	**Vanousheh Rahemi** Hydrogen Peroxide-less Horseradish Peroxidase Based Biosensor for the Detection of Phenols
12:35-12:50	SC03	**Julian Szczesny** Polymer Modified Gas Diffusion Electrodes Containing Hydrogenases or Their Artificial Mimics as Active H_2 Oxidation Catalysts
13:00-14:30		**Lunch**
14:30-16:30		**Afternoon session 1** Chairs: F. Lisdat / J. Szczęsny

14:30-14:50	K09	**Paul A. Millner** Targeted Nanoparticles for Diagnostic and Theranostic Applications
14:50-15:10	K10	**Karolien De Wael** Innovative (Laser Induced) Electrochemical Sensing Strategies
15:10-15:30	K11	**Barbara Jachimska** Development of Dendrimer Based Drug Delivery System
15:30-15:50	K12	**Camelia Bala** Surface Modification for Label-free Sensing
15:50-16:10	K13	**Magdalena Gebala** Dissecting Nucleic Acids Electrostatics - at the Interface of Theory and Experiments
16:10-16:30	K14	**Katarzyna Szot-Karpińska** Label-free Biosensing Platforms based on Bacteriophage Particles for Detection of Diseases Markers
16:30-17:00		**Coffee break**
17:00-18:35		**Afternoon session 2** Chairs: L. Jeuken / E. Lojou
17:00-17:20	K15	**Pawel Krysinski** Surface Properties-dependent Photoelectrochemical Behavior of CdS Nanoparticles
17:20-17:40	K16	**Felipe Conzuelo** Unraveling Photoelectrochemical Processes at Photosystem-based Bioelectrodes by Means of Scanning Photoelectrochemical Microscopy
17:40-18:00	K17	**Alain Walcarius** Electroanalysis with Oriented Nanoporous Silica Thin Films
18:00-18:20	K18	**Zbigniew Stojek** Modification of Electrode Surface with Multifunctional Nano- and Micro-Layers of Materials Sensitive to Environmental Parameters
18:20-18:35	SC04	**Piotr Warszyński** Formation of Casein and Polypeptide in Multilayer Films and Binding of Calcium
19:00-20:00		**Dinner**
20:00-22:00		**Poster session**

T02. **All Will Be Revealed: Mapping Protein Redox Activity with Protein Film Voltammetry**

Julea Butt

School of Chemistry, School of Biological Sciences, University of East Anglia, Norwich, UK.
j.butt@uea.ac.uk

Redox active proteins are ubiquitous in biology. They underpin respiration and photosynthesis, contribute to the synthesis of amino acids and assist in the removal of toxins. Some of these proteins are drug targets, some allow for selective detection of chemicals, others provide inspiration for developing sustainable routes to clean energy and chemicals. As a consequence there is huge interest in understanding protein redox chemistry and exciting opportunities for contributions from dynamic electrochemistry. When proteins exchange electrons directly with electrodes techniques such as cyclic voltammetry can quantify not only reduction potentials, but ligand binding and catalysis. This information is available with particularly high resolution when the protein of interest is adsorbed as an electroactive (sub-)monolayer film on the electrode surface. In such a configuration there is minimal, if any contribution to the voltammetry from protein diffusion, and rate limiting events intrinsic to the protein dominate the response. These aspects of protein film electrochemistry will be illustrated in this contribution. A series of case studies, drawn from experiments on a recently discovered class of protein, will be presented. The benefits of using rotating and stationary electrodes, and experiments with different electrode materials will be explained as a high-resolution map of the protein's redox properties is revealed.

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K03. Multilayered Lipid Membrane Stacks for Biocatalysis Using Membrane Enzymes

George R. Heath,[a] Mengqiu Li,[a] Valentin Radu,[a] Stefan Frielingsdorf,[b] Oliver Lenz,[b] Lars J.C. Jeuken[b]

[a] *School of Biomedical Sciences , University of Leeds, Leeds, LS2 9JT, United Kingdom*
[b] *Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*
L.J.C.Jeuken@leeds.ac.uk

Multilayered or stacked lipid membranes are a common principle in biology and have various functional advantages compared to single-lipid membranes, such as their ability to spatially organize processes, compartmentalize molecules, and greatly increase surface area and hence membrane protein concentration. Here, a supramolecular assembly of a multilayered lipid membrane system is reported in which poly-l-lysine electrostatically links negatively charged lipid membranes. When suitable membrane enzymes are incorporated, either an ubiquinol oxidase (cytochrome bo_3 from *Escherichia coli*) or an oxygen-tolerant hydrogenase (the membrane-bound hydrogenase from *Ralstonia eutropha*), cyclic voltammetry (CV) reveals a linear increase in biocatalytic activity with each additional membrane layer. Electron transfer between the enzymes and the electrode is mediated by the quinone pool that is present in the lipid phase. Using atomic force microscopy, CV, and fluorescence microscopy it is deduced that quinones are able to diffuse between the stacked lipid membrane layers via defect sites where the lipid membranes are interconnected. This assembly is akin to that of interconnected thylakoid membranes or the folded lamella of mitochondria and has significant potential for mimicry in biotechnology applications such as energy production of biosensing.

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K04. **Enzymatic O_2 Reduction on Gold Surfaces: Probing Functional Enzyme Immobilization by Coupling Electrochemistry to SPR, Elllipsometry and PMIRRAS**

V. Hitaishi,[a] S. Lecomte,[b] A. De Poulpiquet,[a] D. Duché,[c] I. Mazurenko,[a] E. Lojou[a]

[a] *Bioénergétique et Ingénierie des Protéines, CNRS-AMU, 31 Chemin Aiguier, 13009 Marseille, France*
[b] *Centre Biochimie des Membranes et Nanoobjets, CNRS, Bordeaux, France*
[c] *Aix Marseille Université, CNRS, IM2NP UMR 7334, 13397 Marseille, France*
lojou@imm.cnrs.fr

Identification and production to purity of redox enzymes from various microorganisms living in very different environments have allowed to envision many of these biomolecules as catalysts in biosensors, bioreactors or bioenergy devices. Among these, one new generation of enzymatic fuel cells is based on very specific enzymes for H_2 oxidation and O_2 reduction, hydrogenase and bilirubin oxidase (BOD) respectively, in replacement of rare and expensive platinum metal, providing a fully sustainable fuel cell. Great improvement has been made during the recent years in the performance of H_2/O_2 enzymatic fuel cells.[1-3] Despite these progresses, two remaining limitations severely limit the large scale development of the biodevices. The first one is the electrical wiring of the enzyme. It was in particular recently shown that less than 10% of the enzymes are in electrical contact with the carbon structure.[4] This issue implies the control of the oriented immobilization of the enzyme to enhance the electron transfer rate and optimize the loading of enzyme at the electrode. The second one is the stability of bioelectrodes. Beyond the research in the biodiversity of more stable enzymes, there is a need to decipher between the various origins for such instability, protein leaching, reorientation, reconformation, denaturation…, then to be able to propose a remediation process.

In this work we present how we have addressed the issues of enzyme wiring and bioelectrode stability by adsorbing BOD and laccase from different origins on thiol-based Self-Assembled-Monolayers (SAM) on gold electrodes.[5-7] SAMs carrying different surface charge and hydrophobicity are used to tune the interaction with the enzymes. pH during enzyme adsorption or during catalysis, and applied potentials are especially studied as factors affecting both the global charge of the enzymes, the charge around the entry point of electrons, and that of the electrode, hence the electrocatalytic process. Coupling electrochemistry to SPR, ellipsometry and PMIRRAS, we establish the correlation between the electrocatalytic current and leaching of the protein or switch in the protein orientation. We discuss the effect of enzyme coverage on the efficiency of the electrocatalysis. We especially highlight the dynamic of enzyme orientation depending on the force of electrostatic interactions. We finally discuss whether the molecular basis obtained on SAMs can be extended to conductive materials such as carbon nanotubes which are mostly required to enhance the biofuel cell performance.[8,9]

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SC01. **Orientation-dependent Direct Electrochemistry of Laccase from *Thermus Thermophilus* Reveals Cuprous Oxidase Activity**

Vivek P. Hitaishi, Romain Clement, Ludovica Quattrocchi, Marianne Ilbert, Elisabeth Lojou, Ievgen Mazurenko

Aix Marseille Univ, CNRS, BIP, UMR7281, 31 chemin Joseph Aiguier, 13402, Marseille, France
imazurenko@imm.cnrs.fr

Multicopper oxidases (MCO) are a group of oxidoreductases containing a couple of Cu-centers: mononuclear T1 and trinuclear T2/T3. These enzymes are able of four-electron oxygen reduction at high potentials reaching 0.78 V (NHE) which is beneficial for different enzymatic and biohybrid fuel cells.[1] A subgroup of MCO called laccases can perform low-specificity oxidation of aromatic compounds which can also be exploited for bioremediation purposes.

In this work we present the electrochemical characterization of the laccase from a hyperthermophilic bacteria *Thermus thermophilus*[2] on CNT-modified electrodes. The as-purified laccase demonstrates direct electron transfer in 4-electron oxygen reduction reaction with current densities that vary significantly depending on the charge and chemical functionalization of CNTs as a consequence of different preferred enzyme orientation.

In addition, we discovered an additional catalytic wave upon the addition of Cu(II) into the electrochemical cell appearing only in the presence of active immobilized laccase. The onset potential and the magnitude of this wave depends on Cu(II) concentration and on the type of CNTs. In homogeneous assays, some MCOs can be activated by addition of Cu(II). Such activation was notably reported for copper efflux oxidase from *E.coli* (CueO), an enzyme responsible for Cu(I) detoxication of the periplasm.[3] Although the exact mechanism and the physiological role of this activation is elusive, it was suggested that it involves Cu(II) binding to the methionine-rich domain near the T1 centre.[4,5] Although the laccase from *Thermus thermophilus* shares only 31% of sequence identity with CueO, a similar methionine-rich domain can be identified suggesting possible Cu(II) binding. We propose that the observed Cu-dependent wave is related to cation binding and cuprous oxidase activity of the laccase. We use electrochemistry to investigate the mechanism of laccase-Cu(II) interaction suggesting that the complexation of additional copper ions creates a new electron pathway within the enzyme molecule.

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K05. **Cytochrome C as Valuable Building Block in Multilayered Architectures of Biocatalysts on Electrodes**

Fred Lisdat

Biosystems Technology, Institute of Life Sciences and Biomedical Technologies, Technical University Wildau, Hochschulring 1, 15745 Wildau, Germany,
flisdat@th-wildau.de

The creation of artificial electron transfer (ET) chains based on the defined arrangement of enzymes and redox proteins on electrode surfaces represents an emerging field in bioelectronics.[1] Precondition for a functional systems exploiting defined electron pathways among the different biocomponents is first of all, a fast heterogeneous electron transfer of the chosen redox protein with the electrode. Furthermore it is beneficial, when interprotein electron transfer is feasible, which is often called self-exchange. Finally, a defined reaction of the biocatalytic units with the chosen redox protein is essential to establish a signal chain from the enzyme substrate via the enzyme and the redox proteins towards the electrode.

For this purpose we have been applying the small redox protein cytochrome c and combining it with several enzymes such as bilirubin oxidase, sulfite oxidase, cellobiose dehydrogenase or fructose dehydrogenase[2-4] or more recently with photocatalytic proteins such as photosystem I.[5]

In case of FDH we have studied the ET reaction of the flavin-dependent enzyme and cyt c first in solution. Here two different pH optima are found for the reaction. When one reaction partner - cyt c - is immobilized on a modified electrode, ET proceeds efficiently at neutral pH. In addition, a defined dependence on the substrate concentration has been observed. In acidic media the reaction can also be verified but appears to be less efficient.

It can be demonstrated that both partners can be assembled in a stable multilayer architecture, using the biopolymer DNA as a negatively charged polyelectrolyte. This can be verified by SPR measurements. Prepared on electrodes, substantial catalytic currents are recorded upon addition of fructose. The response can be enhanced by the number of layers deposited on the surface. This shows that also in this case a signal chain can be constructed through multiple protein layers[4]. Here the interaction of cyt c with DNA as basis of the multilayer construction has been studied in more detail by NMR spectroscopy.[6] Furthermore, the analogy of protein multilayers with cyt c crystals have been evaluedted.[7]

In order to investigate effects influencing the self exchange between different cyt c molecules a mutational study has been performed.[8] Five alanine variants of the wild type protein (Lys→Ala) have been prepared to change the chemical properties of the surface area near the heme edge. The structural integrity of the mutants can be verified by NMR and UV/Vis measurements. It is shown that electro-active protein/silica nanoparticle multilayers can be constructed with all forms of human cyt c prepared. The scan rate dependent voltammetric behavior for the mutant proteins in comparison to the wild type is altered in some multilayer arrangements. A higher self-exchange rate has been found for e.g. K79A. The results demonstrate that the position of the introduced change in the charge situation has a profound influence on the exchange behavior. In addition, the behavior of the cyt c proteins in assembled multilayers is found rather similar to the situation of cyt c self exchange in solution verified by NMR. Based on a model for self exchange also the self exchange rate constants have been estimated, demonstrating that effective electron transfer through defined molecular arrangements of cyt c is feasible.

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K06. Ion Sensors with Coulometric Transduction – Limitations and Possibilities

Tingting Han, Ulriika Mattinen, Zekra Mousavi, Johan Bobacka

Åbo Akademi University, Faculty of Science and Engineering, Johan Gadolin Process Chemistry Centre, Laboratory of Molecular Science and Engineering, Turku/Åbo, Finland
johan.bobacka@abo.fi

Coulometric signal transduction was developed and evaluated for solid-contact ion-selective electrodes (SC-ISEs).[1-5] The SC-ISEs were based on poly(3,4-ethylenedioxythiophene) (PEDOT) as the solid contact and plasticized PVC-based ion-selective membranes. The main goal was to improve the sensitivity of SC-ISEs by using coulometry instead of potentiometry.

For a given change in ion activity and thus a given potential change of the SC-ISE, the magnitude of the measured coulometric signal is proportional to the (redox)capacitance of the solid-contact layer. Therefore, the analytical signal could be amplified by increasing the capacitance of the solid contact.[2] Under optimized conditions, a 0.1 % change in ion activity could be detected when utilizing the coulometric transduction method.[5]

The coulometric method involves charging/discharging of the solid-contact layer of the SC-ISE. Simultaneously, charge-compensating ions must transfer to/from the solid-contact layer via the ion-selective membrane. These processes tend to increase the response time of the SC-ISE. In order to shorten the response time, the electrode resistance was minimized by varying the electrode geometry and by using thin-layer (spin-coated) ion-selective membranes.[3-5] A capacitive model was used to describe the coulometric readout of SC-ISEs.[4]

Limitations and possibilities of the coulometric transduction method for SC-ISEs will be presented and discussed.

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K07. Probing the Interaction of Single Nanoparticle with Interfaces by in Situ Optical Microscopies

Jean-François Lemineur, T. Jane Stockmann, Jean-Marc Noël, Catherine Combellas, Frédéric Kanoufi

Université de Paris, ITODYS laboratory, CNRS UMR 70786, Paris, France
frederic.kanoufi@univ-paris-diderot.fr

The control of the attachment of nanoparticles to surface is ubiquitous in various research and applications fields, from the conception of sensing platform to the building electrode materials for the optimization of charge transport processes in electrochemical energy storage/conversion devices.

Recent analytical and electroanalytical developments propose to apprehend the behavior of nanoparticle systems at the single entity level. In this respect optical microscopies provide an interesting instrumental platform to visualize various nanoobjects, metallic or dielectric, down to 10nm, in a chemical or electrochemical environment. These methods have been used, by us and others, to quantify in situ and real time the electrochemical growth[1] or dissolution of nanoparticles on electrode at the single nanoparticle level.

In this talk we will describe how such optical microscopies can be used to depict the interaction between individual nanoparticles and a surface. This will be presented in the context of microfluidic-based sensors relying on the capture of nanoparticles on a sensing surface[2] or of the electrochemical conversion of nanoparticles.

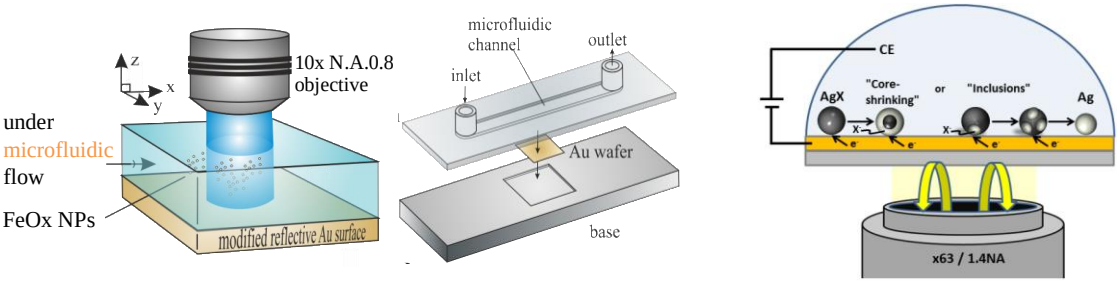

Figure 1. Optical microscopy strategies to probe (left) the capture of nanoparticles by a sensing surface or (right) the role of nanoparticle surface chemistry on their homogeneous or anisotropic electrochemical conversion.

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K08. Enantiodiscrimination at Electrochemical Interphases through Implementation of Inherently Chiral Selectors: New Insights and Perspectives

Patrizia Romana Mussini,[a] Serena Arnaboldi,[a] Sara Grecchi,[a] Mirko Magni,[a] Mariangela Longhi,[a] Vittoria Guglielmi,[a] Francesco Orsini,[a] Emanuela Licandro,[a] Silvia Cauteruccio,[a] Giovanna Longhi,[b] Lorenzo Guazzelli,[c] Roberto Cirilli,[d] Fabiana Arduini,[e] Laura Micheli,[e] Heinrich Lang,[f] Claudio Fontanesi,[g] Simona Rizzo,[h] Tiziana Benincori,[i] Francesco Sannicolò[a]

[a] *Università degli Studi di Milano, Milano, Italy*
[b] *Università degli Studi di Brescia, Brescia, Italy*
[c] *Università degli Studi di Pisa, Pisa, Italy;* [d] *Istituto Superiore di Sanità, Roma, Italy*
[e] *Università degli Studi di Roma Tor Vergata, Roma, Italy*
[f] *Technische Universität Chemnitz, Germany*
[g] *Università degli Studi di Modena e Reggio Emilia, Modena, Italy*
[h] *CNR ISTM, Milano, Italy*
[i] *Università degli Studi dell'Insubria, Como, Italy*
patrizia.mussini@unimi.it

To achieve enantioselective electrochemistry and electroanalysis, electron transfer processes at the electrochemical interphase require the presence of a suitable enantiopure chiral selector, resulting in energetically different diastereoisomeric conditions for the two probe enantiomers.[1] A groundbreaking strategy was recently proposed, based on the use of molecular selectors endowed with "inherently chirality", *i.e.* with chirality and key functional properties originating from the same structural element, which in our case identifies with the main molecular backbone, featuring a tailored torsion with a racemization energy barrier too high to be overcome at room temperature. In such conditions, large peak potential differences have been observed in voltammetry for the enantiomers of even very different chiral probes either (i) working in achiral media, on electrode surfaces modified with thin films of inherently chiral electroactive oligomers[1,2] or (ii) working on achiral electrodes, implementing inherent chirality in the medium, particularly in ionic liquids ILs, either chiral themselves, or modified by a chiral additive,[1,3] exploiting the peculiar IL high order at the interphase with a charged electrode.

Both strategies are being now extended and refined, particularly aiming to collect clues for the elucidation of the recognition mechanism, as well as to highlight attractive applications.

In the film case, advanced techniques are finely highlighting morphology, chemical composition as well as functional properties of inherently chiral electroactive oligomer films, both as electrode surfaces and as self standing membranes. In the media case, chiral and inherently chiral molecules are being studied both as bulk media and/or as media additives, with impressive results. A wide palette of selectors (films or media) and/or probes are being investigated, encompassing four classes of stereogenic elements, *i.e.* corresponding to *stereocentre-based chirality*, *axial chirality*, *helical chirality* and *planar chirality*.

Finally, the outstanding enantiodiscrimination ability of the new selectors is being considered beyond molecular chiral probes, *i.e.* towards *polarized light components* (in terms of circular dichroism and circularly polarized luminescence) and *electron spins* (in magnetoelectrochemistry experiments). Not only impressive effects have been already observed, but fascinating correlations and connections are emerging among the three areas, worthy to be explored in detail, possibly providing further interpretative clues, as well as for possible exploitation in photonics and spintronics.

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SC02. **Hydrogen Peroxide-less Horseradish Peroxidase Based Biosensor for the Detection of Phenols**

V. Rahemi,[a] S. Trashin,[a] Z. Hafideddine,[b] S. Van Doorslaer,[b] V. Meynen,[c] L. Gorton,[d] K. De Wael[a]

[a] *AXES research group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[b] *Laboratory of Adsorption and Catalysis (LADCA), Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium*
[c] *Department of Physics, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium*
[d] *Department of Analytical Chemistry/Biochemistry and Structural Biology, Lund University, PO Box 124, SE-22100 Lund, Sweden*
vanousheh.rahemi@uantwerpen.be

Titanium dioxide (TiO_2)-based enzymatic sensors for the determination of phenolic compounds usually comprise tyrosinase,[1] peroxidase[2] or laccase enzymes.[3] The working principle of these biosensors is based on the redox cycling of a biocatalytic oxidation product of an analyte and the following electrochemical reduction. Hydrogen peroxide (in case of peroxidases) or oxygen (in case of laccase or tyrosinase) plays the role of an ultimate electron acceptor that continuously regenerates the reactive form of the enzyme.[4] Horseradish peroxidase (HRP) is advantageous for developing phenolic biosensors due its high catalytic activity towards a broad range of phenols, but the need of the presence of H_2O_2 in the solution complicates the analysis and increases background noise.[5] Therefore, it is required to develop a hydrogen peroxide-less HRP based biosensor for the detection of phenols.

For the first time we show that TiO_2 can accumulate reactive oxygen species (ROS) under daylight irradiation and can support the catalytic cycle of horseradish peroxidase (HRP) without the need of H_2O_2 to be present in the solution. The ROS act as the sacrificial oxidant or at least produces some amount of reactive species such as H_2O_2, locally and near the site of the enzyme location. Phenolic compounds, such as hydroquinone (HQ) and 4-aminophenol (4-AP), were detected amperometrically in flow-injection analysis mode via the use of an electrode modified with TiO_2 impregnated with HRP. In contrast to the conventional detection scheme, no H_2O_2 was added to the analyte solution. Basically, the inherited ability of TiO_2 to generate ROS is used as a strategy to avoid adding H_2O_2 in the solution during the detection of phenolic compounds. Electron paramagnetic resonance (EPR) spectroscopy indicates the presence of ROS on titania which, in interaction with HRP, initiate the electrocatalysis towards phenolic compounds. The amperometric response to 4-AP was linear in the concentration range between 0.05 and 2 µM. The sensitivity was 0.51 A M^{-1} cm^{-2} and the limit of detection (LOD) 26 nM. The proposed sensor design opens new opportunities for the detection of phenolic traces by HRP-based electrochemical biosensors, yet in more straightforward and sensitive way.

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SC03. Polymer Modified Gas Diffusion Electrodes Containing Hydrogenases or Their Artificial Mimics as Active H_2 Oxidation Catalysts

Julian Szczesny,[a] Felipe Conzuelo,[a] Sónia Zacarias,[b] Inês A. C. Pereira,[b] Wolfgang Lubitz,[c] Adrian Ruff,[a] Wolfgang Schuhmann[a]

[a] *Analytical Chemistry – Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr-University Bochum, D-44870 Bochum, Germany.*
[b] *Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, 2780-157 Oeiras, Portugal.*
[c] *Max-Planck-Institut für Chemische Energiekonversion, Stiftstrasse 34-36, D-45470, Mülheim an der Ruhr, Germany.*
julian.szczesny@rub.de

The use of highly active but highly sensitive non-noble metal catalysts for energy conversion, i.e. hydrogenases or DuBois-type catalysts for H_2 oxidation is limited by their fragility and the difficulties to connect such catalysts to electrode surfaces. The incorporation of these catalysts into redox polymers overcomes these limitations and the redox polymers simultaneously provide a hydrophilic immobilization matrix and an electron relay matrix that shuttles electrons between the active catalyst and the electrode surface. Moreover, by using low potential redox polymers, air-sensitive catalysts can be protected by the in-situ reduction of incoming O_2 at the polymer electrolyte interface.[1]

However, in (bio)electrochemical devices based on flat and non-porous electrode systems the diffusional mass transport of the gaseous substrates typically limits the catalytic current due to their low solubility in aqueous media. Hence, fabrication of high current density (bio)electrodes is still a major challenge. The use of gas diffusion electrodes is a promising approach to overcome this limitation. Within these electrodes a three-phase boundary at the electrolyte-catalyst-gas interphase is established to ensure a high local substrate flux and thus high substrate concentrations at the catalytically active sites.

The combination of the benefits of redox polymers, i.e. protection of sensitive catalysts and high catalyst loading with the concept of a gas diffusion electrode (enhanced mass transport) is supposed to ensure high current densities which are desired for the fabrication of high performance (bio-)fuel cells.

In this contribution, we present a dual gas-breathing H_2/air biofuel cell that is equipped with a H_2 oxidizing bioanode consisting of a hydrogenase embedded in specifically designed redox polymers, coupled to a conventional O_2 reducing, bilirubin oxidase-based biocathode operating in a direct electron transfer regime. The biofuel cell exhibits an open circuit voltage of 1.13 V and delivers an outstanding power output of 3.6 mW cm^{-2} at 0.7 V, setting a benchmark for redox polymer/hydrogenase based biofuel cells.[2] Furthermore, we transposed the concept for polymer based gas diffusion electrodes including the protection and wiring ability to an artificial and highly active but also O_2-sensitive DuBois-type catalyst for successful H_2 oxidation.[3]

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K09. Targeted Nanoparticles for Diagnostic and Theranostic Applications

Paul A. Millner, Shazana H. Shamsuddin, Arindam Pramanik, Arwen I. Tyler, Yazan Khaled, Darren C. Tomlinson, P. Louise Colletta, David G. Jayne

University of Leeds, UK

p.a.millner@leeds.ac.uk

Targeted nanoparticles provide an exciting opportunity for delivery of drugs to specific tissue locations but also for imaging and sensing applications. Many drugs, and in particular chemotherapy agents, are too toxic to deliver systemically, but when packaged into nanoparticles and directed to a specific target off-target effects are avoided and a much higher doses are delivered. The same nanoparticles can carry fluors and other imaging agents and in some case can act both to image solid tumours and also to deliver therapy. Work will be described using antibodies[1,2] and synthetic binding proteins, Affimers[3,4] against the biomaker protein CEA[1] to target nanoparticles to colorectal cancer cells, both in 2D culture and as 3D spheroids and in mouse xenograft models. Targeting of silica nanoparticles, bearing fluors for imaging or photosensitizers for photodymanic therapy, and of lipidic cubosomes[5] loaded with hydrophobic organo-copper cytotoxins results in specific and efficient imaging and cell killing of cancer eells but not control (non-cancer) cells. The immobilisation chemistries involved to tag the bioreceptor (targeting agent) to the nanoparticle surface will be discussed.

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K10. **Innovative (Laser Induced) Electrochemical Sensing Strategies**

Karolien De Wael

Antwerp University, AXES research group, 2020 Antwerp, Belgium
karolien.dewael@uantwerpen.be

Today the demand for ultra-sensitive and selective on-site detection systems resounds from the health, food and environmental sector. These systems must be able to detect and quantify target molecules, important in point-of-care testing and for assessing the level of contamination in food and environmental samples for example. Electrochemical sensors are very attractive for monitoring the presence and concentration of pollutants as these devices are fast, portable and extremely sensitive and selective towards electro-active species.

After a short introduction on general activities, innovative concepts in electrochemical sensing will be discussed by focusing on topics with high societal and industrial relevance (e.g. drugs of abuse, antibiotics, antigens).

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K11. **Development of Dendrimer Based Drug Delivery System**

Barbara Jachimska

Jerzy Haber Institute of Catalysis and Surface Chemistry
Polish Academy of Sciences, Kraków, Poland,
ncjachim@cyf-kr.edu.pl

Previous experimental studies confirm that dendrimers, due to their unique physical and chemical properties resulting mainly from their structure, have high application potential.[1] Particularly interesting is the use of these systems as drug carriers in molecular targeted therapy. The dendrimer structure potentially allows two types of therapeutic agent immobilization: in a multilayer dendrimer shell or inside the molecular structure. Since the biggest problem of many drugs is their low water solubility, dendrimers were designed with water-soluble terminal groups and hydrophobic interiors, which leads to the encapsulation of hydrophobic drugs. Understanding the nature of dendrimer-drug interaction is essential for understanding the molecular mechanism of system optimization and control. The study of dendrimer-drug complex formation in physiological conditions using a wide range of analytical methods allows optimizing the physicochemical properties of nanosystems in terms of the efficiency of drug accumulation and release.[2,3]

Nanoparticles entering biological systems are almost always covered with biofluids. Thus, to develop an effective system of selective drug delivery, it is necessary to understand the mechanism associated with the change of conformation and competition of proteins to the surface of the carrier. The interaction of functional materials with various types of proteins present in plasma, along with the analysis of conformational changes and reorganization of protein structures have a high cognitive value.[4]

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K12. Surface Modification for Label-free Sensing

Camelia Bala

University of Bucharest, Department of Analytical Chemistry, Bucharest, Romania
camelia.bala@chimie.unibuc.ro

This lecture intends to be an overview on the research activity developed by our group in the sensing field, especially the design of the interface between the physical transducer and the biological recognition elements. The immobilization of the active biological component on the transducer surface represents a critical stage in the biosensors development and it has as a goal the settlement of the bioactive part on the surface of the physical transducer. The chosen immobilization procedure has to keep the biological component in the native conformation. On the other hand the physical transducers should have an adequate sensitivity toward the species to be detected.

The lecture will illustrate the practical applications of surface modification of electrochemical and SAW sensors, focusing on layer-by-layer assembly and thiol-driven self-assembly and sol-gel chemistry, grafting chemistries including click chemistry and practical applications from environmental and biomedical analysis areas.[1-4]

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K13. Dissecting Nucleic Acids Electrostatics - at the Interface of Theory and Experiments

Magdalena Gebala

Department of Biochemistry, Stanford University, Stanford, CA 94305 USA
mgebala@stanford.edu

Nucleic acids are one of the most charged polymers in nature, carrying two negative charges per base pair. Hence, the molecules generate a strong negative electrostatic field that influences their mechanical properties and their interactions with other molecules. This field also plays a critical role in modulating the orientation of tethered nucleic acids at electrified interfaces, as well as other processes such as hybridization, dehybridization and recognition of small molecules, which are key components in designing biosensors and other engineering applications.[1-3]

Despite, the fundamental important of electrostatic interactions in structure and function of nucleic acids, they are poorly understood. The primary barrier to progress is the lack of experimental approaches to quantitatively study interactions between macromolecules and the ions required to mitigate their charge and to correlate these effects with their energetic consequences. Importantly, the clear majority of ions that play this role are not site-specifically bound, but rather are part of a highly mobile and intrinsically disordered cloud of ions, which is referred to as the ion atmosphere.

I will present an experimental approach, buffer equilibration–mass spectroscopy (BE-MS), that 'counts' the number of ions thermodynamically associated with a macromolecule or complex, allows dissection of energetic properties of the ion atmosphere, and provides direct comparison to theoretical results.[4] I will show an additional new experimental approach that provides a local electrostatic meter, determining the electrostatics surface potential of DNA molecule.[5] I will also discuss electrochemical studies on effects of electrostatic field on thermodynamics and kinetics of DNA hybridization at electrified interfaces.[3]

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K14. Label-free Biosensing Platforms based on Bacteriophage Particles for Detection of Diseases Markers

Katarzyna Szot-Karpińska

Institute of Physical Chemistry Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
kszot@ichf.edu.pl

A constant search for new applicable materials in electrochemical sensors and electronic devices encourages scientists turn towards interdisciplinary research. Particularly interesting in this context is the combination of biology with chemistry and material sciences. Recently, bacteriophages (phages - viruses that infect bacteria) are increasingly used in electrochemical applications, e.g. as recognition elements in biosensors to develop new sensing platforms for medical applications or as templates to create new electrode materials for batteries and biofuel cells.[1-3]

In our studies we are applying phage particles, antibodies, carbon nanomaterials and the phage display technique for the detection of various disease markers e.g. the thiol biomarker L-cysteine[4] and C-reactive protein (CRP). This is investigated using electrochemical, optical and biological methods. Also microscopic techniques (AFM, SEM, and TEM), and spectroscopic analysis (UV-Vis, IR, and XPS). The phage display technique is used to isolate new receptor (bacteriophages/peptides) that specifically recognize CRP – a marker of inflammatory processes in the human body. The new binding receptor obtained within our studies could become a long sought-after superior alternative to traditional used antibodies and can be utilized as artificial antibodies for the differentiation between viral and bacterial infections.

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K15. **Surface Properties-dependent Photoelectrochemical Behavior of CdS Nanoparticles**

Momoka Nagamine,[a] Magdalena Osial,[b] Justyna Widera-Kalinowska,[b] Krystyna Jackowska,[b] Pawel Krysinski[b]

[a] *Department of Chemistry, Adelphi University, One South Avenue, Garden City, NY 11530, USA*
[b] *Faculty of Chemistry, University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland*
pakrys@chem.uw.edu.pl

CdS nanoparticles with either hydrophilic or hydrophobic properties were synthesized via hydrothermal method. Oleylamine (OA) in hexane was used as a capping agent resulting in hydrophobic nanoparticles. Morphology of synthesized nanoparticles was characterized by SEM, their hydrodynamic size and zeta potential were determined by DLS dynamic light scattering. UV-vis spectroscopy was used to determine their band gap energy.

Comparative photoelectrochemical studies of hydrophilic, drop-casted CdS nanoparticles and 10, 20 and 50 Langmuir-Blodgett layers of hydrophobic CdS nanoparticles deposited on ITO were performed after immersing in SO_4^{2-}/SO_3^{2-} redox couple solution. The electron lifetime in both hydrophilic and hydrophobic nanocrystalline CdS was determined. The observed longer carrier lifetime for oleylamine-capped CdS nanoparticles can be assigned to the interface between the organic shell and nanoparticle core and by the resistance of this shell against the flux of charges. Photocurrent of CdS L-B electrodes depends on the number of deposited layers and increases with the number of layers. Substantial hindrance of photopotential and photocurrent was observed for those films as compared to the hydrophilic, uncoated nanoparticles drop-casted directly on ITO and we assign this result to the impaired flux of charges due to the presence of organic shell.

K16. Unraveling Photoelectrochemical Processes at Photosystem-based Bioelectrodes by Means of Scanning Photoelectrochemical Microscopy

Fangyuan Zhao, Adrian Ruff, Wolfgang Schuhmann, Felipe Conzuelo

Analytical Chemistry – Center for Electrochemical Sciences, Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsstr. 150, D-44780, Bochum, Germany
felipe.conzuelo@rub.de

Owing to their remarkable abundance and high quantum efficiency, the biological photosystems are particularly interesting building blocks for the fabrication of biophotovoltaic devices. Coupling of photosynthetic protein complexes with electrodes enables the development of semi-artificial devices aiming for an efficient and cost-effective solar-to-chemical energy conversion. For an optimized electron transfer and operation of the assembly, an adequate integration of the isolated redox proteins into implemented photoelectrochemical devices is required. To date, several reports have shown the design of advanced architectures and engineered electron transfer chains enabling the coupling of isolated photosynthetic proteins with various electrode surfaces. However, different factors inherent to the complex nature of such biomolecules make the design of photosystem-based devices particularly challenging. For instance, the possibility for short-circuiting processes as a result of the large voltage difference between opposite redox sites generated upon light-induced charge separation compromises the effective extraction of photocurrents. Moreover, light-induced damage under certain experimental conditions may cause degradation of the biological components with a consequent drop in activity over time, substantially limiting the applicability of biohybrid devices. Thus, a better understanding of charge recombination pathways and electron transfer processes is essential to enable the development of state-of-the-art devices with an improved and highly efficient performance. In this context, scanning photoelectrochemical microscopy (SPECM) has proven to be a powerful tool for the desired extensive evaluation of photosystem-based semi-artificial devices and diverse photoactive electrode architectures.[1-4] In this technique, an accurately positioned microelectrode is coupled to a light source enabling local illumination of the analyzed sample surface. As a result, it is possible to monitor local photoelectrocatalytic reactions with the microelectrode tip acting simultaneously as the electrochemical probe in a sample generator/tip collector arrangement. As it will be presented, this technique is a versatile tool for the local evaluation of photoelectrochemical processes at the micro scale. Examples including the analysis of biological photosystems integrated in suitably designed redox polymers will be shown, providing a better understanding of charge recombination pathways and electron transfer processes towards the development of more efficient biophotovoltaic devices.

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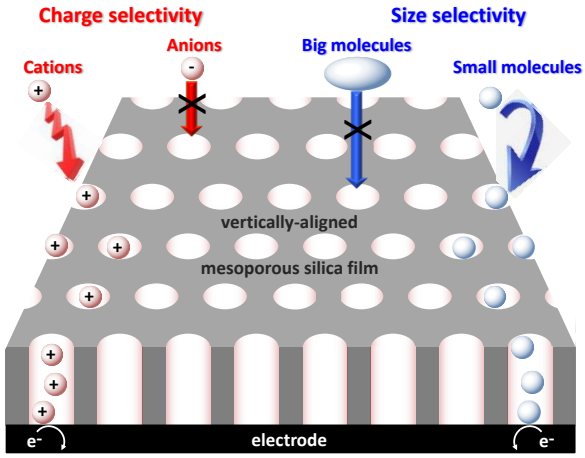
K17. **Electroanalysis with Oriented Nanoporous Silica Thin Films**

Alain Walcarius

Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement (LCPME) – UMR7564 CNRS – Université de Lorraine, 405 rue de Vandoeuvre, 54600 Villers-les-Nancy, France
alain.walcarius@univ-lorraine.fr

Nanoporous silica thin films consisting of highly ordered and vertically aligned nanochannels have received considerable research interest in the past years, notably because they guarantee great molecular accessibility and fast mass transport.[1] They are also characterized by size and charge permeability properties (scheme 1).[2-4] As deposited onto electrode surfaces, they are very promising for various applications, in particular in electroanalysis.[5-7]



Scheme 1. Illustration of charge and size selectivity at vertically aligned mesoporous silica film.

This lecture will summarize and highlight (i) the main synthesis strategies to get oriented mesoporous silica films on electrodes; (ii) their basic permselective properties and factors likely to affect them; (iii) the way to functionalize them to give the corresponding organic-inorganic hybrid membranes; (iv) their applications in the field of electrochemical analysis with emphasis on preconcentration electroanalysis, protection against (bio)fouling, electrocatalysis and long-range charge transport.

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K18. Modification of Electrode Surface with Multifunctional Nano- and Micro-Layers of Materials Sensitive to Environmental Parameters

Kamil Marcisz, Klaudia Kaniewska, Marcin Mackiewicz, Marcin Karbarz, Zbigniew Stojek

Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland
stojek@chem.uw.edu.pl

Polymeric hydrogels became attractive mainly because of their ability to perform a reversible phase transformation that is associated with a large change in their volume and triggered by a change in environmental conditions. A big research effort was directed to extension of the list of such environmental parameters and to modification of the phase transformations. In this respect the changes in temperature, ionic strength and pH, substitution of the crosslinker, use of additional monomers in the synthesis, and the presence of some ions can be mentioned. A clear trend is emerging: it is the synthesis of hydrogels of micro and nano sizes.[1,2] It is mainly associated with a significant reduction of phase-transformation time and facilitation of reaching, by ions and molecules, the deep inside and outside of the gel. Progress in hydrogel deposition on conductive surfaces can be useful in a number of issues; it can lead to an improvement in the construction of artificial muscles and it can also improve the performance of biosensors and the ON-OFF systems in microfluidic systems and *labs on chips*.

This presentation focuses on discussion of various ways of modification of electrodes/conductive-materials with nano- and micro-hydrogels. The main emphasis will be given to electrodeposition of very thin layers and chemisorption of spherical nanoparticles. The electrochemical properties of the electrodes modified with the hydrogels in various ways differ a lot. They particularly differ in their response to volume phase transition. The conditions have been found for the electrochemical induction of the volume phase transformation at the surface of an electrode.[3] After the introduction of either amino ferrocene or hexaamino ruthenium(III)/(II) system into the hydrogel, it was possible to trigger the phase transition by applying an appropriate potential. In addition, the change in microgel size / volume using the electrochemically induced volume phase transition was significant and reversible. It also turned out that thin hydrogel films are very convenient matrices for enzymes.

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SC04. **Formation of Casein and Polypeptide in Multilayer Films and Binding of Calcium**

Lilianna Szyk-Warszyńska, Zofia Krasińska-Krawet, Katarzyna Raszka, Piotr Warszyński

Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Kraków, Poland
ncwarszy@cyf-kr.edu.pl

Multilayer films containing α- and β-casein and polypeptides, poly-L-lysine (PLL) and poly-L-arginine (PLArg) were formed by the layer-by-layer technique at various pH conditions, and their infrared spectra were analyzed by FTIR-ATR and FTIR/Grazing Angle.[1] We investigated changes of conformations of casein and polypeptides in the surface complexes formed during the build-up of the films and after contacting them with $CaCl_2$ solutions. Additionally, we performed molecular dynamics simulations of the systems consisting of short PLL and PLArg chains and the representative peptide chains – casein fragments, consisting of several aminoacid sequences to establish the differences in the mechanism of complex formation leading to various growth of $(PLL/casein)_n$ and $(PLArg/casein)_n$ films. Analysis of the FTIR spectra revealed greater conformational changes during the formation of casein complex with poly-L-arginine than with poly-L-lysine that was accompanied by a larger growth of $(PLArg/casein)_n$ films thickness/mass with the number of deposited layers. That could be explained by the results of the simulation indicated the preferential formation of hydrogen bonds of poly-L-arginine with phosphoserine and glutamic acid residues of caseins. Variation of the FTIR spectra in the wavelength region corresponding to PO_3^{2-} symmetric and asymmetric vibration with the films immersion time in with $CaCl_2$ solutions provided evidence of calcium ions binding within the multilayer films by the embedded phosphoserine residues in particular at pH 7.4. At pH 5.5 more favorable growth of multilayers with β-casein was observed and Ca^{2+} were preferentially bound to glutamic acid residues, whereas at pH 8.6 only a minor changes in the FTIR were observed indicating lower ability of caseins embedded in the multilayers to bind calcium.

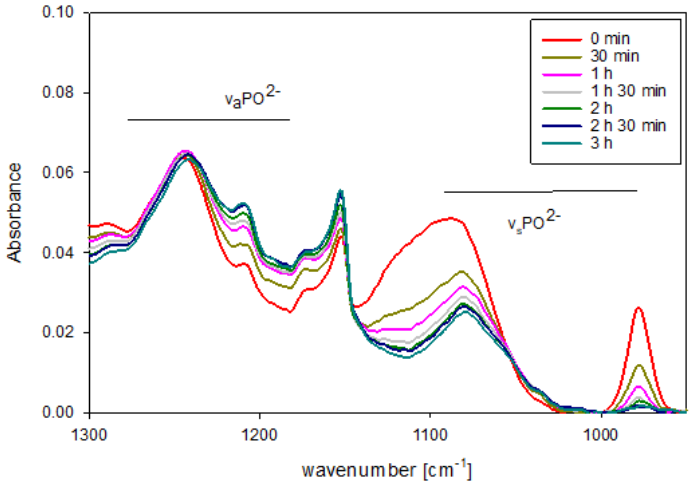

Figure 1. Changes of the FTIR spectrum of α-casein/PLArg multilayer upon contact with 50 mM $CaCl_2$ solution at pH 7.4.

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Sunday, November 10

08:00-09:00		**Breakfast**
09:00-10:35		**Morning session 1** Chairs: P. Krysiński / J. Bobacka
09:00-09:40	T03	**Francis D'Souza** Interfacial Electron Transfer of Multimolecular Assemblies on Metal Oxide Semiconductors
09:40-10:00	K19	**Frank Marken** Polymers of Intrinsic Microporosity (PIMs) in Electrochemistry
10:00-10:20	K20	**Stéphane Arbault** Using Cold Plasmas to Improve Electrochemical Sensors and vice versa
10:12-10:35	SC05	**Krzysztof R. Noworyta** Oxidation and Coupling of the Selected Carbazole Derivatives – Why It Does Not Always Lead to Polymer Formation
10:35-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: K. Noworyta / A. Yarman
11:00-11:20	K21	**Karsten Haupt** Molecularly Imprinted Polymer Nanoparticles as Synthetic Antibody Mimics for the Detection and Modulation of Cellular Function and Immunotherapy
11:20-11:40	K22	**Frieder W. Scheller** Electrosynthesized MIPs for Peptides and Proteins
11:40-12:00	K23	**Peter A. Lieberzeit** From Self-organized Monolayers to Surface Molecular Imprints: Assay Formats Extending Beyond the Obvious
12:00-12:20	K24	**Cédric Ayela** Combining Molecularly Imprinted Polymers (MIPs) with Micro (Opto) Electro Mechanical Systems (M(O)EMS) for Improved Chemical Sensing
12:20-12:35	SC06	**Yasuo Yoshimi** Application of Swelling Phenomena of Molecularly Imprinted Polymers by Specific Interaction with the Target Molecule for Sensing Technology
12:35-12:50	SC07	**Cecilia Cristea** Biomimetic Approaches over Direct Detection of Antibiotics from Real Samples
13:00-14:30		**Group Photo & Lunch**
14:30-16:20		**Afternoon session 1** Chairs: R. Gyurcsanyi / F. Conzuelo
14:30-14:50	K25	**Pawel J. Kulesza** Development of Highly Specific Interfaces for Photoelectrochemical and Electrocatalytic Reduction of Carbon Dioxide

14:50-15:10	K26	**Ambra Giannetti** A Fluorescence-based POCT Device for Immunosuppressant-drug Monitoring in Transplanted Patients
15:10-15:30	K27	**Joanna Niedziółka-Jönsson** Long-Period Fiber Gratings for Sensing and Biosensing
15:30-15:50	K28	**Sebastian Maćkowski** Sensing with Plasmonically Active Metallic Nanostructures
15:50-16:05	SC08	**Wolfgang Fritzsche** Localized Surface Plasmon Resonance (LSPR) on Metal Nanoparticles for Bioanalytical Applications
16:05-16:20	SC09	**Simone Berneschi** Optical Microbubble Resonators as Emerging Tools for Environmental Sensing: the “Safe Water” Project

16:30-19:00 Social program

19:00-22:00 Dinner/Banquette

T03. **Interfacial Electron Transfer of Multimolecular Assemblies on Metal Oxide Semiconductors**

Francis D'Souza

Department of Chemistry, University of North Texas, Denton, TX 76203, USA
Francis.Dsouza@unt.edu

Semiconducting metal oxide nanoparticles offer a unique substrate for the assembly of multiple, photoactive, molecular components at the interface. The choice of photoactive molecules, nature of semiconducting metal oxide (p-type or n-type), and the type of the assembly method (covalent versus self-assembly), and nature of spacer connecting the photoactive molecules to the surface, can have a profound influence on the mechanism, rate, and efficiency of photoinduced energy and electron transfer events at the interface. The variety and high level of control, these interfacial assemblies are of interest for many applications including solar energy harvesting, optoelectronics, photo-electrosynthesis, photo-sensing, photo-writable memory, and more. These assemblies, although, are generated with different end goals, they rely on similar surface binding motifs and molecular structure-property relationships. The goal of this tutorial talk is to summarize the various strategies (i.e. covalent binding, axial coordination, ion-ion and ion-dipole electrostatics, host-guest interactions, etc.), developed mainly from our laboratories, for assembling chromophores, hosts, and electron donors/acceptors on mesoporous metal oxide substrates and conducting electrode surfaces. The assembly, characterization, and subsequent photoinduced events (i.e. cross-surface electron transfer, interchromophore energy transfer, electron injection and recombination, and others), relevant to dye sensitized solar cell applications, will be discussed for the various assembly approaches.

K19. **Polymers of Intrinsic Microporosity (PIMs) in Electrochemistry**

Frank Marken,[a] Neil B. McKeown[b]

[a] *Department of Chemistry, University of Bath, Bath BA2 7AY, UK*
[b] *School of Chemistry, University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, Scotland EH9 3JJ, UK*
F.Marken@bath.ac.uk

Polymers of Intrinsic Microporosity (PIMs) provide a novel class of structurally rigid potentially semi-permeable membrane materials with 3D nanofluidic pores of typically 1.5 nm size. The PIM-EA-TB material was employed to protect nanoparticle catalysts, and in a membrane cell configuration as a pH-dependent semi-permeable anion-conductor. When deposited asymmetrically over a 20 μm diameter hole in poly-ethylene-terephthalate (PET) and investigated in a two-compartment electrochemical cell with aqueous electrolyte on both sides, ionic diode effects[1] are observed. Potential for applications in electrocatalysis and in electroanalysis are associated with the molecularly rigid polymer structure. Other types of PIMs such as PIM-1 and PIM-7 (see Figure 1) allow "gas management" under triphasic reaction conditions at electrocatalyst surfaces, e.g. at palladium, and photo-electrochemical processes.[2]

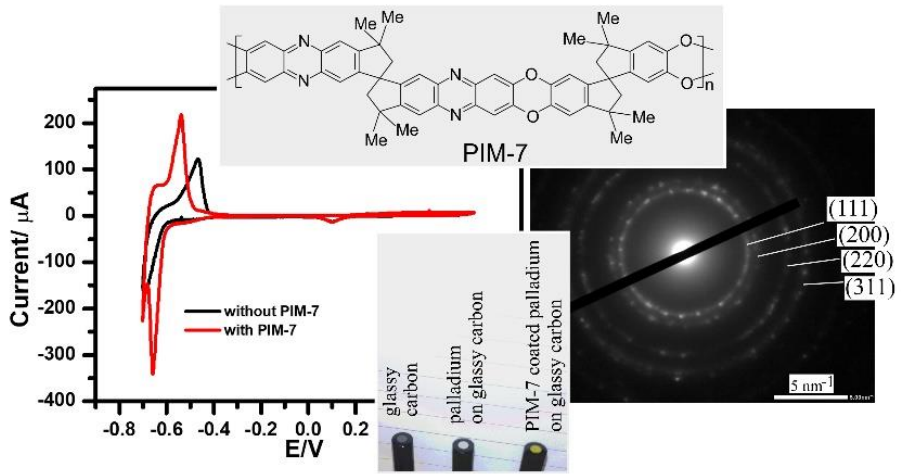

Fig. 1. Molecular structure of PIM-7 and cyclic voltammetry data for nano-palladium deposited onto glassy carbon with/without a PIM-7 coating.

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K20. **Using Cold Plasmas to Improve Electrochemical Sensors and *vice versa***

Colin Camille,[a] Badets Vasilica,[a] Girard Fanny,[a,b] Lefrançois Pauline,[a] Botsos-Margerit Ugo,[a] Zigah Dodzi,[a] Blanc Sylvie,[b] Sojic Neso,[a] Clément Franck,[b] Arbault Stéphane[a]

[a] *Univ. BORDEAUX, ISM, Bordeaux INP, CNRS UMR 5255, NSysA Group, Pessac, France*
[b] *UPPA, IPREM, CNRS UMR 5254, Pau, 64000, France*
stephane.arbault@u-bordeaux.fr

Cold plasmas are weakly ionized gases, generated by applying High-Voltage electrical discharges in a gaseous environment. They can be produced by sinusoidal or pulse power supplies, at either low pressures (ex. mTorr) or in ambient conditions depending on the electric field intensity as well as on the used gas (mixtures of N_2, O_2, Ar, He, methane etc.). Cold plasmas are complex mixtures of neutral species, electrons, ions, excited species (radiative and metastable states, radicals…) and emitted photons (UV, Vis, IR). In particular, when generated in oxygen-nitrogen mixtures (air), multiple reactive oxygen and nitrogen species (ROS, RNS) are present in the gas phase. Because of their diverse and intense reactivities, and relative ease for production, cold plasmas reveal themselves as excellent approaches to treat surfaces in order to modify their physical (cleaning, roughening) and chemical (functional groups) states.

In this context, we applied cold plasmas to modify the reactivity of metal and carbon electrode surfaces and studied the resulting effects on the detection of compounds involved by biosensors.[1,2] We first treated platinum and black platinum modified electrodes by 100 % Oxygen-plasmas produced by radio-frequency modulated electric fields (plasma cleaner setup) and observed lower capacitive currents, more stable faradaic responses, decreased standard potentials and improved sensitivity for H_2O_2 detection. These properties were related (XPS analyses) to a change of ratio between Pt oxides, which improve the surface hydrophilicity and initial adsorption of ROS. Similarly, the reactivity of glassy carbon electrodes could be homogenized and improved for the detection of both inner- or outer-sphere electron transfer species when treated by plasmas, allowing to prevent from polishing electrode surfaces for their cleaning or activation. Moreover, plasma effects were stable for periods longer than one week.

Reciprocally, such electrochemical sensors were involved to decipher on the nature of species produced by cold atmospheric pulsed plasmas when used to expose physiological fluids, cells or tissues.[3-5] Plasmas raise exponential interests for biomedical applications because of their strong reactivities. However, the true nature of reactive species involved in biocidal or oxidative bio-activation remains widely unsolved. To decipher on the *in situ* reactivity within solutions exposed to plasmas, we developed shielded microelectrodes to detect ROS and RNS appearing in solution, at millimetric distances from the plasma flow and electric source (nanosecond pulsed discharges). The concentration rises of hydrogen peroxide, nitrite as well as of superoxide anion were monitored with an unprecedented spatial and temporal resolutions.[6]

Consequently, we have demonstrated that electrochemical sensors can benefit from plasma treatments and *vice versa*.

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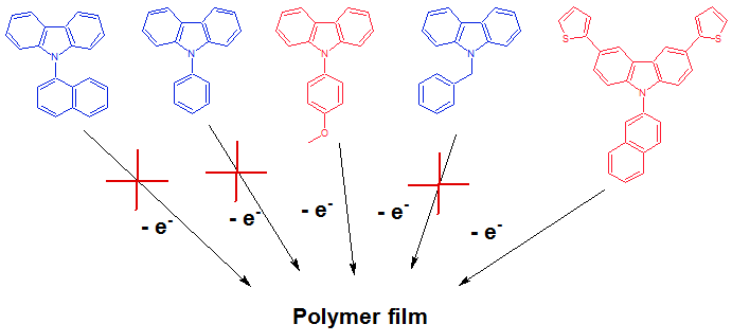
SC05. **Oxidation and Coupling of the Selected Carbazole Derivatives - Why It Does Not Always Lead to Polymer Formation**

Jyoti,[a,b] Renata Rybakiewicz,[c] Teresa Żołek,[d] Dorota Maciejewska,[d] Krzysztof R. Noworyta[a]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*
[c] *Faculty of Mathematics and Natural Sciences, School of Sciences, Cardinal Stefan Wyszynski University in Warsaw, Woycickiego 1/3, 01-815 Warsaw, Poland,*
[d] *Department of Organic Chemistry, Faculty of Pharmacy, Warsaw Medical University, Banacha 1, 02-097 Warsaw, Poland*
knoworyta@ichf.edu.pl

Carbazole and its derivatives are large class nitrogen-containing aromatic heterocyclic compounds. Because they exhibit a large π-conjugate system, rigid fused rings, and desirable electronic and charge transport properties they are widely studied and used as dyes, photoelectrical materials, supramolecular recognition, and medicinal agents.[1] Additionally, they can be easily and conveniently functionalized with large variety of functional groups introduced both into the carbazole rings or nitrogen atom.



Recently a library of carbazole derivatives modified with aromatic moieties at nitrogen atom, with and without thiophene substituents at C-3 atom has been synthesized. Synthesis was performed in view of they use as functional monomers in fabrication of molecularly imprinted polymer films via electrochemical deposition. The synthesized monomers have been characterized by UV-vis spectroscopy, fluorescence studies and voltammetry. Surprisingly, some of the monomers did not form polymer films upon electrochemical oxidation, while still being electrochemically active.

In this contribution, we present results of investigations of the observed behavior. In order to better understand the effect we have performed quantum-chemistry calculations of the monomers capable and incapable of electropolymerization. The calculation results were subsequently compared with electrochemical, spectroscopic and spectroelectrochemical experiments. Collected data allowed rationalization of the observed electrochemical behavior of the synthesized monomers.

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K21. Molecularly Imprinted Polymer Nanoparticles as Synthetic Antibody Mimics for the Detection and Modulation of Cellular Function and Immunotherapy

Karsten Haupt, Paulina Medina Rangel, Jingjing Xu, Bernadette Tse Sum Bui

Université de Technologie de Compiègne, CNRS Institute for Enzyme and Cell Engineering, Compiègne, France
karsten.haupt@utc.fr

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

Herein, we demonstrate the potential of MIPs for immunotherapy on the example of a protein cancer biomarker, a cell-cell recognition protein.[3] In addition, we present the use of MIPs for the inhibition or modulation of cell-virus interactions.[4]

MIPs were synthesized using an innovative solid-phase synthesis approach in which an epitope of the biomarkers was immobilized on glass beads (as solid support) via click chemistry. This configuration allows an oriented immobilization of the template. A short peptide (terminal alkyne or azide functionalized) was selected as epitope for immobilization on azide-modified glass beads. The epitope was either a terminal peptide sequence, or an internal peptide. In the latter case, a cyclic version of the peptide was used as the template. Thermo-responsive MIP nanoparticles were synthesized around the template. Due to the oriented immobilization of the latter, the binding sites of the resulting MIPs all have the same orientation and a homogeneous affinity distribution in the nanomolar range, thus MIPs synthesized by the solid-phase approach can be considered analogous to monoclonal antibodies. The MIP nanoparticles (50 nm) specifically recognized both the template peptides and the whole proteins. Mutation of a single amino acid in the peptide sequence resulted in a reduced affinity by three orders of magnitude.

Cell imaging studies were done with fluorescently labeled MIP nanoparticles, using epifluorescence and confocal fluorescence microscopy. They showed specific binding of the synthetic antibody to the cell surface targets, since the non-imprinted control polymer did not show any staining, and when the target protein was hydrolytically removed from the cell, staining was dramatically decreased. They were able to modulate specific cellular functions.

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K22. **Electrosynthesized MIPs for Peptides and Proteins**

Frieder W. Scheller,[a] Aysu Yarman,[a] Xiaorong Zhang,[a] Katharina J. Appelt,[a] Ulla Wollenberger,[a] Giorgio Caserta,[b] Ingo Zebger,[b] Goksu Ozcelika,[c] Sevinc Kurbanoglu,[c] Sibel A. Ozkan,[c] Róbert E. Gyurcsányi[d]

[a] *Universität Potsdam, Institute for Biochemistry and Biology, Potsdam, Germany*
[b] *Technische Universität Berlin, Inst. für ChemieBerlin, Germany*
[c] *Ankara University, Dept. of Analytical Chemistry, Ankara, Turkey,*
[d] *Budapest University of Technology and Economics, Budapest, Hungary*
fschell@uni-potsdam.de

Molecular imprinting is a method to create binding cavities in a polymer for the preferential recognition of the target. Here, we present two approaches for electrosynthesizing protein-MIPs using scopoletin or o-phenelenediamine as the functional monomers.

(i) Epitope imprinting: MIPs for the recognition of the N-terminal peptides of human adult hemoglobin (HbA) or glycated Hb (HbA1c) were synthesized by applying either the mixtures of scopoletin and the respective terminal pentapeptides or a SAM of the cys-extended N-terminal pentapeptide of the ß-chain in the MIP synthesis by electropolymerizing scopoletin on the gold electrode. These two peptides are the analytes in the IFCC (the International Federation of Clinical Chemistry) Reference Method for the determination of the long-term biomarker for diabetes HbA1c. All steps of MIP-synthesis and rebinding were analyzed by square wave voltammetry (SWV) of the redox marker ferricyanide and by surface-enhanced infrared absorption (SEIRA) spectroscopy of both the bound target, i.e., the peptides or the parent protein, and the polymer poly-scopoletin. Combination of the respective MIPs allows the quantification of both the glycated and the non-glycated N-terminal peptides of HbA1c and HbA.

(ii) Holoprotein as target: MIP-sensors for the copper containing enzymes laccase and tyrosinase, cytochrome P450cam and butyrylcholineesterase were prepared by electropolymerizing the mixture of monomer and target protein. For these highly active enzymes, synthesis of holoprotein-MIPs is the straightforward approach.

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K23.

From Self-organized Monolayers to Surface Molecular Imprints: Assay Formats Extending Beyond the Obvious

Agienszka Strallhofer,[a] Chakpetch Koitio,[b] Supaporn Klangprapan,[b] Kiattawee Choowongkomon,[b] Peter A. Lieberzeit[a]

[a] *University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria*
[b] *Faculty of Science, Department of Biochemistry, Kastesart University, Bangkok, Thailand*
Peter.Lieberzeit@univie.ac.at

Sensing and analysis are among the main driving forces of developing novel responsive surface modifications. To avoid the limitations of biological species, they often make use of different biomimetic approaches.[1] Many of those approaches rely on self-organization at some point, for instance by immobilizing recognition species (such as aptamers) on sensor surfaces, or generating surface molecularly imprinted polymers (MIP).

Molecularly imprinted polymers[2] have proven useful for selectively binding biological species ranging from proteins to entire cells.[3] One often assumes that they do so by forming non-covalent interactions with a part of the outer surface of the respective target species. It is possible to assess this claim by comparing the sensor responses of different selective surfaces on similar devices with each other. Studies on the porcine respiratory and reproductive syndrome virus (PRRSV) with aptamers and surface MIP revealed that the former gave rise to somewhat higher selectivity toward two competing species (porcine respiratory virus – PRV; common swine fewer virus – CSFV). However, surface MIP led to ten times higher sensitivity of the respective coated quartz crystal microbalances (QCM). Both results indicate that aptamers indeed bind to clearly defined "receptor" sites, whereas MIP interact with the entire outer shell of the virus. Selectivity of MIP relies on two different factors, namely geometric fit and surface chemistry, respectively.

Similar comparative studies revealed that both MIP and immobilized thrombin are useful for binding thrombocytes to the respective sensor surface, be it a QCM or an SPR substrate (SPR: surface plasmon resonance). The main challenge from the imprinting side in this case is given by the fact that it is by far not trivial to generate stamps comprising native, i.e. non-activated thrombocytes. However, overcoming this obstacle allowed us to design sensor materials that give rise to concentration-dependent responses when exposed to different platelet concentrates. Response times are in the range of around ten minutes. Though this is slower than current cell counting systems, MIP sensors have one main advantage: sensor signals do not only depend on cell concentration, but also on the status of thrombocytes: exposing them to anti-coagulants changes the chemical properties of their surfaces. This leads to decreased sensor effects due to lower affinity to the respective MIP. We could reproduce such behavior with thrombin immobilized to SPR chips. Therefore, such sensors allow for assessing the status of the respective cells. Within about ten minutes, one can hence assess the coagulation ability of the respective cells, which is much faster than in current clinical diagnostics.

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K24. Combining Molecularly Imprinted Polymers (MIPs) with Micro (Opto) Electro Mechanical Systems (M(O)EMS) for Improved Chemical Sensing

Cédric Ayela,[a] Frank Bokeloh,[a] Olivier Soppera,[b] Karsten Haupt[c]

[a] *Univ. Bordeaux, IMS, CNRS, UMR 5218, Bordeaux INP, ENSCBP, Talence, France*
[b] *IS2M, CNRS, UMR 7361, Univ. Haute Alsace, Mulhouse, France*
[c] *Sorbonne Universités, UTC, CNRS, GEC UMR 7025, Compiègne, France*
cedric.ayela@ims-bordeaux.fr

Molecularly imprinted polymers (MIPs) are tailor-made antibody mimics obtained by a templating process at the molecular level. These tailor-made polymers have, unlike their natural biological counterparts, a superior chemical and physical stability and are therefore excellent candidates for integration into sensors and biochips. Over the years, we have reported several strategies of micro (opto) electro mechanical systems (M(O)EMS) with integrated MIP pattern, using different micro- and nanofabrication techniques for the synthesis of 2D and 3D MIP-based sensors. First, we showed the combination of MIPs with resonant silicon micromembranes enabling the label-free detection of low molecular weight analytes, by means of mass sensing.[1] To go further, we have then reported an all-organic sensor consisting in a simple monolayered free-standing MIP microcantilever, used once again as mass sensor.[2] Merging the mechanical transducer and the MIP film into a single device reduces the total mass of the device, one important characteristic to increase their mass sensitivity. Results showed the sensitive and specific binding of the beta-antagonist drug S-propranolol. In particular, a limit of detection of 100nM was achieved, a successful challenge for label-free mass sensors. More recently, the technique of 2-photon stereolithography was used to fabricate 2.5D MIP diffraction gratings and 3D MIP microcantilevers in a single step.[3] The synthesis of MIPs by 2-photon stereolithography enables the fabrication of real 3D structures with a sub-micrometer resolution and overcomes the limitations of standard 2D microstructures. Diffraction and resonance frequency measurements allowed demonstrating specific analyte binding (testosterone and Z-L-Phenylalanine) to diffraction gratings and microcantilevers, respectively. Last, but not least, we showed very recently that MIP microcantilevers can be synthesized directly at the end of optical fibers.[4] This technique was introduced by Ton et al. using the polymer tip as a fluorescence sensor, that we have adapted for label-free, mass sensing using the resonance of the MIP tip.[5] With this approach, the same optical fiber is used for both the fabrication of a polymer beam at its cleaved end, and the dynamic mode operation of the cantilever. In particular, optomechanical coupling enables both actuation of the MIP cantilevers and detection of the resonance, enabling remote sensing over long distances. This approach is of particular interest for the development of mass-produced chemical sensors, to be exploited at industrial level.

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SC06.

Application of Swelling Phenomena of Molecularly Imprinted Polymers by Specific Interaction with the Target Molecule for Sensing Technology

Y. Yoshimi, H. Eguchi, Y. Takeda, M. Abe, and Y. Katsumata

[a] *Department of Applied Chemistry, Shibaura Institute of Technology Tokyo, Japan*
yosimi@sic.shibaura-it.ac.jp

It has been shown that the faradic current at an electrode grafted with molecularly imprinted polymer (MIP) is sensitive to the specific target molecule used as the template.[1] This phenomenon termed "gate effect" is applicable to sensors with very high selectivity and short response time. For example, gate effect of heparin imprinted MIP is sensitive to heparin but insensitive to chondroitin sulfate C (CSC) which has similar structure as heparin. The response time is less than 60 s.[2] But the sensing mechanism is still in a black box. We investigated the size sensitivity of nanoparticles of molecularly imprinted polymers (MIP-NPs) to a specific interaction for determination of the mechanism of the gate effect and its feasibility for new applications.[3] Nanoparticles of poly(methacryloxy ethyl trimethylammonium chloride-*co*-acrylamide-*co*-methylenebisacrylamide) imprinted with heparin immobilized on glass beads were synthesized. The diameter of the MIP-NPs of heparin was increased by the presence of the heparin template but was insensitive to CSC, the analogue of heparin. The high selectivity of the MIP-NPs was consistent with the selectivity of electrodes grafted with a heparin-imprinted polymer in our previous studies. The quartz crystal microbalance probes immobilizing heparin or CSC were sensitive to MIP-NPs, which indicates that the binding ability of MIP-NP does not discriminate between the template and other glycosaminoglycans. These results indicate that the size of the MIP-NP is sensitive to the matched binding with the template through the imprinted cavity and confirm that the sensors using the gate effect of MIP enable more highly specific sensing of the targets used as a template than those detecting the targets bound with MIP directly. The MIP-NP would be potential tool for understanding the mechanism of the gate effect. As an expanded the application of MIP-NP, we revealed that the MIP-NP can be used as an optical probe which can visualize the secretion of the target secreted from cells.[4]

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SC07. Biomimetic Approaches over Direct Detection of Antibiotics from Real Samples

Adrian Blidar, Bogdan Feier, Oana Hosu, Gheorghe Melinte, Mihaela Tertis, Cecilia Cristea

Department of Analytical Chemistry, Faculty of Pharmacy, "Iuliu Haţieganu" University of Medicine and Pharmacy, 4 Pasteur Street, 4000349, Cluj-Napoca, Romania
ccristea@umfcluj.ro

There are numerous analytical methods for the detection of different classes of antibiotics, but most of them are relatively expensive and require complex laboratory instruments, leading to the impossibility to perform field analyses. Electrochemical techniques are a viable alternative due to their sensitivity and accessibility, both from an economical and logistical point of view, making them suitable for *in situ* analysis, a big advantage for environmental and clinical tests.[1] *β*-lactam antibiotics are the most important and the most widely used group of antibiotics, consisting mainly of two subclasses, penicillins and cephalosporins. Tetracyclines (TCs) are one of the most common used antibiotics for the treatment of infectious diseases in veterinary medicine. Therefore, high TCs levels can be found in animal-based food products (*e.g.* meat, eggs, milk) and environmental samples (*e.g.* soil, waste water) due to its high accumulation. The overuse of this therapeutic class, for prophylactic and treatment purposes, but also in agriculture, assures a constant exposure, increasing the risk of allergies and resistance to broad-spectrum antibacterial drugs. A part of the solution for this concerning situation is the development of new and rapid detection methods capable of monitoring the levels of antibiotics from different matrices.[1,2]

Using direct approaches, we tested the electrochemical behavior of several members of the penicillins and cephalosporins classes, recording their electrochemical signals, but this way was unable to distinguish between molecules from the same subclass. However, using this approach, the quantification of cefalexin (CFX) and oxacillin was performed.

In order to surpass the limitations in terms of selectivity and sensitivity, the biomimetic approaches were employed by using molecularly imprinted polymers (MIPs) and aptamers (short single-stranded DNA and RNA oligonucleotides, artificially selected for their capacity to bind specifically a target molecule). The biomimetic approach improved the detection of CFX, both in terms of selectivity and sensitivity, leading to the development of an electrochemical MIP-based sensor for CFX. Another biomimetic strategy allowed the detection of ampicilin using an electrochemical surface plasmon resonance aptasensor. AMP direct detection was proved to be unsuccessful due to the low value of the response and also due its similarity to the response of other penicillins.[2] As for the direct detection and quantification of tetracycline, gold was electrodeposited at glassy carbon electrodes and carbon-based screen-printed electrodes from a $HAuCl_4$ solution to obtain different 3D-nanostructures (nanoparticles and nanovoids). A ferrocene-labelled aptasensor for TC detection was developed using the platform with the best analytical performance.

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K25. Development of Highly Specific Interfaces for Photoelectrochemical and Electrocatalytic Reduction of Carbon Dioxide

Pawel J. Kulesza, Iwona A. Rutkowska

Faculty of Chemistry, University of Warsaw, Poland

Electroreduction of carbon dioxide to simple organic fuels and chemicals is a topic of growing scientific and technological interest. The reaction provides means for both reducing emissions of CO_2 into atmosphere and storing renewable energy. The presentation will address low-temperature CO_2-conversion processes based on electrocatalytic and photoelectrochemical approaches. Among important issues are choice of the catalytic or semiconducting materials, their morphology and operating conditions including temperature, solvent, electrolyte, pH etc. There is a need to improve the reaction dynamics and selectivity toward specific products. In practical electrolysis cells, the CO_2-reduction (at cathode) is accompanied by water oxidation (at anode or photoanode).

Recently, we have concentrated on the development of hybrid materials by utilizing combination of metal oxide semiconductors thus capable of effective photoelectrochemical reduction of carbon dioxide. For example, the combination of conducting polymers, or titanium (IV) oxide, and copper (I) oxide has been considered before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH_3OH) as demonstrated upon identification of final products. Among important issue is intentional stabilization, activation, and functionalization of the mixed-metal-oxide-based photoelectrochemcal interface toward better long-term performance and selectivity production of small organic molecules (C1-C4) and other chemicals. In this respect, ultra-thin films of conducting polymers (simple or polyoxometallate-derivatized) and supramolecular complexes (with nitrogen containing ligands and certain transition metal sites), sub-monolayers of metals (Cu, Au), networks of noble metal (Au, Ag) nanoparticles or layers of robust bacterial biofilms have been considered.

K26.

A Fluorescence-based POCT Device for Immunosuppressant-drug Monitoring in Transplanted Patients

A. Giannetti,[a] S. Tombelli,[a] C. Trono,[a] S. Berneschi,[a] C. Berrettoni,[a] F. Baldini,[a] R. Bernini,[b] I. A. Grimaldi,[b] G. Testa,[b] G. Persichetti,[b] G. Porro,[c] G. Quarto[c]

[a] *CNR-IFAC "Nello Carrara" Institute of Applied Physics, 50019 Sesto Fiorentino (FI), Italy*
[b] *Institute for Electromagnetic Sensing of the Environment - CNR, Napoli, Italy*
[c] *Datamed S.r.l., Peschiera Borromeo (MI), Italy*
a.giannetti@ifac.cnr.it

In the treatment of transplanted patients, therapeutic drug monitoring represents one of the most crucial aspects for the identification of the correct dosage of immunosuppressants, aiming to ensure the appropriate medical treatment and to avoid the rejection of the transplanted organ.[1] Recent clinical studies have demonstrated that the better clinical indication for the correct drug administration is provided by the area under the concentration-time curve (AUC) of immunosuppressants, since this value is better correlated with efficiency and potential side effects than the through level. Since only protein-unbound (free) drugs can cross membranes and bind to receptors to produce the required pharmacological effect, free drug concentrations (2-8% for immunosuppressive drugs) are more closely related to efficacy and also to toxicity compared to plasma, serum or whole blood concentrations, better reflecting the clinical outcome.

At this aim, a novel point of care testing (POCT) optical device for the detection of blood immunosuppressant free fraction in transplanted patients was designed and tested, with the body interface constituted by an intravascular microdialysis catheter (MicroEye®), which provides the dialysate as clinical sample. The work was undertaken in the framework of the EU project NANODEM (NANOphotonic DEvice for Multiple therapeutic drug monitoring). The benefit of this device will be an optimized dosage of the therapeutic drugs to support patient management in a clinical environment.

In order to reach the low limit of detection required by the clinicians and enable the detection of the therapeutic drug free fraction, a heterogeneous binding inhibition immunoassay has been developed, in a microfluidic chip, with the use of antibody-coated polystyrene particles decorated with magnetic ferrite nanograins doped with the fluorescent dye BODIPY-641. The microfluidic optical chip, based on total internal reflection fluorescence (TIRF) and on fluorescence anisotropy, is constituted by an array of microfluidic channels the surface of which is chemically modified with the analyte derivative. The excitation light, coming from an external source, is properly coupled and confined by TIRF into the optical waveguide constituting the chip, and is guided towards the sensing area.

Calibration curves for cyclosporine A (CyA) and mycophenolic acid (MPA) in dialysis perfusate (20% Lipofundin) were obtained with limit of detection for CyA and MPA of 0.48 ng/mL and 0.79 ng/mL, respectively. In addition, real clinical Lipofundin-based microdialysate samples, each containing CyA and MPA, were tested and results were compared with a novel liquid chromatography–tandem mass spectrometry (LC-MS/MS) method that was developed within the course of the NANODEM project at the Institute of Clinical Chemistry and Pathobiochemistry, Klinikum rechts der Isar der TU München.

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K27. **Long-Period Fiber Gratings for Sensing and Biosensing**

Marta Janczuk-Richter,[a] Mateusz Śmietana,[b] Wojtek J. Bock,[c] Joanna Niedziółka-Jönsson[a]

[a] *Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland*
[b] *Institute of Microelectronics and Optoelectronics, Warsaw University of Technology, Warsaw, Poland*
[c] *Centre de recherche en photonique, Université du Québec en Outaouais, Canada*
jniedziolka@ichf.edu.pl

The biosensor market is developing fast in recent years mainly due to the growing demand for point-of-care devices and fast detection solutions that may be applied in healthcare, biodefence, environmental monitoring, and food industry. Significant improvements have been made in optical label-free biosensors that provide fast, simple, and accurate analysis. Another advantages, such as small size, low cost, and flexibility, can be obtained by using optical fiber sensors. Here, we present sensors and biosensors based on long-period fiber gratings (LPFGs).

LPFG is a periodic modulation of refractive index (RI) of the core of single-mode optical fiber with a grating period in the order of hundreds of micrometers. This perturbation leads to phase matching between fundamental core mode and forward propagating cladding modes. It results in several attenuation bands in the transmitted spectrum which positions depend on the RI of the external medium, as well as the thickness and optical properties of the film/overlay formed on the LPFG surface.

High sensitivity of LPFGs to external RI (~2000 nm/RIU), that indicates also label-free sensing capabilities, was obtained by chemical etching of the surface cladding. Additionally, the surface drying effect on optical response of LPFG was analyzed.[1] The results showed that drying done between measurements performed in liquid significantly influences transmission spectrum of LPFG due to the changes in the cladding surface. This indicates that any drying should be avoided because it may cause getting misleading conclusions. Therefore, the flow cell in which the surface drying is limited was designed and used for other measurements with LPFG-based sensors.

The sensitive LPFGs were used for preparation of highly demanded biosensors for virus detection. First, surface modification methods for receptor immobilization were tested. Vapor phase silanization was used to introduce proper functional groups on the surface. The best tested protocols were further used for preparation of biosensors. By application of antibody-modified LPFG it was possible to detect 5 x 10^3 PFU/mL of T7 bacteriophages[2] and 1 ng/mL of norovirus virus-like particles in 40-min assay. Moreover, the method of surface regeneration, which may decrease production costs and enable conducting different measurements on the same LPFG sensor, was presented.

Finally, we demonstrated the usefulness of thin metal oxide overlays. Tantalum oxide film was used for the sensitivity enhancement and indium tin oxide coated LPFG was used to perform simultaneous optical and electrochemical measurements.[3,4]

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K28. **Sensing with Plasmonically Active Metallic Nanostructures**

Sebastian Maćkowski[a,b]

[a] *Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland*
[b] *Baltic Institute of Technology, Gdynia, Poland*
mackowski@fizyka.umk.pl

Metallic nanostructures, which feature plasmon resonances in the visible spectral range, can be used for efficient detection of fluorescent species, provided they arrive in sufficient proximity to facilitate strong plasmonic coupling. In this regard, silver nanowires (AgNWs) and silver island film (SIF) structures are particularly attractive, as they feature plasmon resonances that span over the whole visible range down to near infrared.

The presentation will focus on several examples of using either AgNWs or SIF as platforms for detecting biological species. While silver nanowires are chemically stable in both water and buffer solutions, can be obtained using straightforward wet chemistry synthesis, as well as their surface can be functionalized appropriately, silver island films can be fabricated in a controlled way on several surfaces of interest, such as glass, ITO, plastic, and alike, without compromising the enhancement ability. In this way, both types of metallic nanostructures are suitable for fluorescence imaging of specific conjugation, either in solution or in real-time upon deposition on surfaces.

In conclusion, the comprehensive experimental evidence indicates that geometry constrain with proper surface functionalization, when combined with strong enhancement of the optical response, make both AgNWs and SIF considerably attractive nanostructures for fast and specific sensing.

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SC08. Localized Surface Plasmon Resonance (LSPR) on Metal Nanoparticles for Bioanalytical Applications

David Zopf, Angelina Pittner, Cornelia Reuter, Philipp Müller, Ondrej Stranik, Andrea Csaki, Wolfgang Fritzsche

Leibniz Institute of Photonic Technology (IPHT) Jena, Germany
wolfgang.fritzsche@ipht-jena.de

Metal nanostructures exhibit interesting optical properties based on localizedon localized surfaecsurface plasmon resonance (LSPR), due to interactions of irradiated light with conduction electrons.[1] This property depends on inherent properties of the nanostructures like composition, size and geometry, but is also influenced by the refractive index of the surrounding. The latter effect is used for sensing purposes, by using highly specific complementary biomolecules for bioanalytical applications[2] such as DNA-based detection of pathogens. Target molecule binding will result in a local increase in refractive index leading to a resonance shift, which represents the sensoric signal that is readout spectroscopically.

Different aspects of bioanalytical applications of LSPR will be presented, such as both top-down (nanosphere lithography)[3] as well as bottom-up (chemical synthesis including microfluidics)[4] generation of metal nanostructures as sensors, including preparation of dedicated assay substrates e.g. in a microarray arrangement,[5] and the subsequent biofunctionalization with DNA in order to realize a highly specific biosensor. Towards the optical detection, both single-particle[6] as well as imaging spectroscopic readout of arrays[7] will be demonstrated. A multiplexed DNA-based pathogen detection scheme based on LSPR is presented,[8] as well as an approach to use gold nanoparticle aggregation for a simple and robuste DNA detection also for low resource settings.

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SC09. **Optical Microbubble Resonators as Emerging Tools for Environmental Sensing: the "Safe Water" Project**

S. Berneschi,[a] F. Baldini,[a] A. Giannetti,[a] G. Nunzi Conti,[a] S. Pelli,[a] S. Tombelli,[a] C. Trono,[a] F. Bettazzi,[b] I. Palchetti,[b] Z. Chen,[c] G. Barillaro,[c] L. Ferrante Vero,[d] S. Neri,[d] G. Virgili,[d] L. Derszi,[e,f] J. Mazuryk,[e] P. S. Sharma,[e] W. Kutner,[e] P. Jorge,[g] P. Marques[g]

[a] *CNR-IFAC "Nello Carrara" Institute of Applied Physics, 50019 Sesto Fiorentino (FI), Italy*
[b] *Chemistry Department, University of Florence, 50019 Sesto Fiorentino (FI), Italy*
[c] *Information Engineering Department, University of Pisa, 56122 Pisa (PI), Italy*
[d] *West Systems S.r.l., 56025 Pontedera (PI), Italy*
[e] *IPC-PAS Institute of Physical Chemistry Polish Academy of Sciences, 01-224 Warsaw, Poland* [f] *ScopeFluidics, 01-796 Warsaw, Poland*
[g] *INESC-TEC, 4200-465 Porto, Portugal*
s.berneschi@ifac.cnr.it

In the last decades, the rapid growth of the world population and the increase in industrial and agricultural activities have contributed to a continuous depletion of the water resources quality, endangering the health of individual citizens especially when water is destined for human consumption. As highlighted in recent European directives on the quality and monitoring of the water environments (EU 2013/39, EU 2015/495 and EU 2018/840), particular attention is paid to emerging microcontaminants (EMCs such as drugs, hormones, personal care and life-style products), which, even if present in traces in the aqueous matrices, are poorly biodegradable and difficult to remove through conventional treatment processes.[1,2] Then, once these contaminants are entered within these aqueous matrices, they remain there and their presence can cause known or suspected adverse ecological and/or human health effects.[3]

Therefore, it becomes essential to have an analytical method that can detect the presence of these pollutants at low concentrations. Based on the synergy among different competences of the consortium partners in the field of chemistry, electronics, photonics, microfluidics, the aim of the SAFE WATER project is the realization of a new portable optical instrument for in situ and multiplexing detection of different EMCs. The core of the device consists in the use of whispering gallery mode (WGM) optical microbubble resonators (OMBRs), considered as a localized swelling induced in a silica microcapillary by a suitable fabrication process.[4] These hollow-core resonant microcavities support the exclusive properties of the WGM resonators (i.e.: small mode volumes, high Q factor values, typically > 10^7 in air, high analytical sensitivity and extremely low limit of detection LOD up to pg/L) with an embedded microfuidics and their sensing principle is generally based on a label-free strategy.[5]

The achievement of this innovative monitoring system requires the realization of the following objectives: *i*) development of an OMBR matrix, integrated on a chip, as an optical transduction element capable of detecting the selected EMCs in parallel; *ii*) development of chemical/biochemical functionalization protocols in order to modify the OMBR inner surface using highly specific chemical biochemical receptors for the selected EMCs; *iii*) development of the microfluidic circuit for mixing and sending the liquid sample with its chemical reagents to the OMBR matrix; *iv*) development of the optoelectronic system for interrogation of the OMBR matrix and for data processing and management.

In this presentation the general aspects of the project and its progress will be presented and discussed.

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Monday, November 11

08:00-09:00		**Breakfast**
09:00-10:35		**Morning session 1** Chairs: A. Giannetti / Y. Yoshimi
09:00-09:40	T04	**Gary J. Blanchard** Interfacial Free Charge Density Gradients in Room Temperature Ionic Liquids and Their Potential Applications
09:40-10:00	K29	**Ilaria Palchetti** Novel Materials for Electrochemical Biosensing of Nucleic Acids
10:00-10:20	K30	**Gerd-Uwe Flechsig** Detection of DNA Cross-linking with Cisplatin by Redox-switching of DNA Viscoelasticity Using EQCM
10:20-10:35	SC10	**Elena V. Suprun** Electrocatalytic Sensing of Protein and DNA Molecules on Prussian Blue Modified Electrodes
10:35-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: K. Haupt / S. Arbault
11:00-11:20	K31	**Marcin Opałło** Scanning Electrochemical Microscopy Detection of the Hydrogen Peroxide and Hydrogen Generated at Liquid-Liquid Interface
11:20-11:40	K32	**Wojciech Nogala** Nanoscale Mapping of Chemical and Biochemical Activity at Modified Surfaces
11:40-12:00	K33	**Stefania Rapino** Functional Imaging of Cellular Processes Using Scanning Electrochemical Microscopy
12:00-12:20	K34	**Vitali Syritski** Molecularly Imprinted Polymers Interfaced with Label-free Transducers: towards Development of Chemosensors for Medical Diagnostics and Environmental Monitoring
12:20-12:35	SC11	**Aysu Yarman** Epitope-MIP for Engineered Enzymes
12:35-12:50	SC12	**Yulia Efremenko** Electrical Control of the Receptor Affinity
13:00-14:30		**Lunch**
14:30-16:25		**Afternoon session 1** Chairs: P. Lieberzeit / C. Cristea
14:30-14:50	K35	**Alexander Kuhn** Electronic Diversion of Enzymes for Carrying Out Unconventional Tasks

14:50- 15:10	K36	**Mathieu Etienne** Bacterial Biocomposite Materials: a Tool for Optimizing and Studying Extracellular Electron Transfer Reactions
15:10- 15:30	K37	**Tautgirdas Ruzgas** Wireless, Battery-less Biosensor Tags Based on Direct Electron Transfer Reactions
15:30- 15:50	K38	**Ulla Wollenberger** Bioelectrocatalysis and Bioanalytical Applications of Molybdoenzymes
15:50- 16:10	K39	**Sławomir Sęk** Electron Transport in Nanoscale Junctions with Helicomimetic Foldamers
16:10- 16:25	SC13	**Łukasz Półtorak** Simple Methods for the Electrified Liquid – Liquid Interface Downscaling. From Design to Sensing Applications
16:25-17:00		**Coffee break**
17:00- 18:25		**Afternoon session 2** Chairs: W. Nogala / S. Rapino
17:00- 17:20	K40	**Insung S. Choi** Single-cell Nanoencapsulation
17:20- 17:40	K41	**Jenny Emnéus** 2D and 3D Lab-on-a-Chip Systems for Life Science Applications
17:40- 17:55	SC14	**Maciej Cieplak** Protein imprinting. Better control over deposited polymer structure for better sensor performance.
17:55- 18:10	SC15	**Aleksandra Jaworska** Towards SERS-based Detection of DNA Mutations
18:10- 18:25	SC16	**Lidia J. Opuchlik** About Gold Nanotriangles and Their Applications
19:00-20:00		**Dinner**
21:00-		**Disco**

T04. **Interfacial Free Charge Density Gradients in Room Temperature Ionic Liquids and Their Potential Applications**

Gary J. Blanchard

Michigan State University, Department of Chemistry
578 S. Shaw Lane
East Lansing, MI 48824 USA

We have reported the existence of long range order (*ca*. 100 μm) in room temperature ionic liquids (IL) which is induced by the surface charge of the support on which a film of ionic liquid resides. This long range order can be modulated by the support surface charge, providing facile control over the sign and magnitude of the gradient with respect to the surface normal. Our recent work has demonstrated such control as well as the effect of water on the existence of the gradient. Our findings indicate that the chemical structure of the ionic liquid constituents can play an important role in mediating the role of water in this class of materials. Current work is focused on devising novel nonlinear optical strategies for characterization of the charge density gradient with an eye toward their utilization in interfacial sensing applications.

K29. Novel Materials for Electrochemical Biosensing of Nucleic Acids

Ilaria Palchetti

Dipartimento di Chimica Ugo Schiff, Università degli Studi di Firenze, Sesto Fiorentino (FI), Italy

In comparison with other techniques, bioelectroanalytical sensors permit the analysis of clinically relevant species with great specificity and very rapidly, being sensitive, highly selective and, in principle, cheap. In particular, electrochemical genosensors have been intensively studied due to their potential for nucleic acid testing, as a result of their appropriate sensitivity, multiplexing capability, and small amount of sample required.

However, the electrocatalytic activity, the electron transfer kinetic and the chemical reactivity of the electrode material as well as the electrode surface area itself, can affect the biosensor sensitivity and selectivity and can direct the choice of the detection scheme. Indeed, in order to find the optimal biosensing strategy, the properties of the electrode surface can be modulated, by using novel materials.

Herein, different approaches based on the use of functional nanostructures and conducting polymers will be discussed. Recently, we have optimized *in situ* colloidal chemistry approaches to achieve a high density and very uniform coverage of reduced graphene oxide (RGO) nanoflakes with Au nanoparticles (NPs). Graphene is an interesting platform for electrochemical sensing. In particular, its high chemical reactivity makes it a robust scaffold for manufacturing original and highly functional hybrid nanocomposite materials with inorganic NPs and by non-covalent methods, exhibiting enhanced properties that the pristine components do not intrinsically possess. The electrochemical behavior of these novel AuNPs-RGO nanostructures, have been investigated towards the electrochemical sensing of clinically relevant molecules and towards the development of DNA-based biosensors.[1]

Moreover, we have also evaluated approaches based on the use of conducting polymers for electrochemical and photoelectrochemical sensing of nucleic acids with emphasis on biocompatible systems and herein preliminary results will be discussed.[2]

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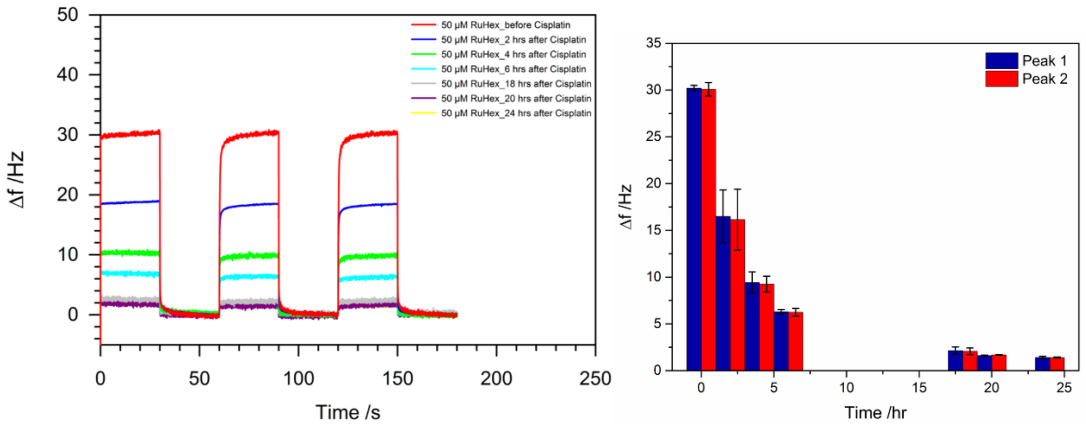
K30. Detection of DNA Cross-linking with Cisplatin by Redox-switching of DNA Viscoelasticity Using EQCM

Gerd-Uwe Flechsig,[a,b] Sarasi K. K. Galagedera[b]

[a] *Coburg University of Applied Sciences, Coburg, Germany*
[b] *University at Albany – SUNY, Albany, NY, USA*
gerd-uwe.flechsig@hs-coburg.de

Recently we have reported on quick changes of the viscoelasticity of DNA layers immobilized on gold electrodes observed as a response upon redox-switching of ruthenium complexes at the millisecond time scale by means of electrochemical quartz crystal microbalance (EQCM).[1] We have now applied this new approach with single stranded and double stranded DNA/ 6-mercapto-1-hexanol (MCH) mixed SAMs on gold electrodes in the presence of hexammine ruthenium(III) (RuHex) to monitor the DNA crosslinking-modification with cis-diammine dichloroplatinum(II) (cisplatin). Our new EQCM studies confirmed that the redox response of electrostatically bound RuHex is capable of providing quantitative information regarding the extent of DNA cross-linking with cisplatin.



The Figure illustrates a time study of decreasing EQCM frequency response of a DNA layer after crosslinking reaction with 100 µM cisplatin in 10 mM $NaClO_4$ followed by the redox-switching experiment with 50 µM RuHex in 10 mM Tris buffer at pH 7.5. **Left**: EQCM frequency signals obtained upon redox-switching with RuHex. **Right**: EQCM frequency response at different reaction times with cisplatin.

The drop in EQCM frequency response can probably be interpreted as a loss of viscosity switching ability caused by the crosslinking of DNA strands. The effect was observed with both ssDNA and dsDNA. Sequence of DNA oligos also plays a role.

We believe that this method can be used in studies to test the interactions of cancer chemotherapeutic medications like cisplatin with DNA and ultimately be a new technology for rapid screening of potential drug candidates and their interactions with DNA in order to inhibit cancer cell growth by forming DNA adducts.

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SC10. **Electrocatalytic Sensing of Protein and DNA Molecules on Prussian Blue Modified Electrodes**

Elena V. Suprun,[a] Elena V. Karpova,[b] Sergey P. Radko,[a] Arkady A. Karyakin[b]

[a] *Institute of Biomedical Chemistry, Pogodinskaya Street, 10/8, 119121, Moscow, Russia*
[b] *Chemistry Faculty of M.V. Lomonosov Moscow State University, Lenin Hills, 1/3, 119991, Moscow, Russia*
lenasuprun@mail.ru

The detection of biopolymers such as proteins and DNAs, is of a great significance for fundamental and applied biomedical studies as well as medical diagnostics. These macromolecules play crucial roles in biological processes, both in health and disease, and serve in many instances as disease markers. Electrochemical detection of proteins and DNAs through the direct redox reactions of their monomeric units, side chains of amino acid residues and nucleotides (direct electrochemistry) benefits from the simplicity, low cost, speed, and potential for miniaturization, thereby making it especially suitable for 'point-of-care' or 'in-field' testing. Moreover, direct electrochemistry allows one to detect biomolecular conformational changes, mutations, ligand binding, oxidative damage, and post-translational modifications.[1-3]

At present, it is generally accepted that in proteins only Tyr, Trp, His, Met, Cys, and Cys-Cys residues can be electrochemically oxidized on solid (carbon) electrodes,[2,3] while in DNA molecules all nucleobases (G, A, T, and C) are known as electoactive.[1,4] On carbon electrodes, the oxidation of protein and DNA molecules takes place at relatively high positive potentials (0.5 V and higher). The major drawback of direct biopolymer electrochemistry is a low level of registered currents. It is suggested that the specific electrocatalytic oxidation of amino acids and nucleobases may allow to overcome these problems.

In this work, the electrochemical oxidation of protein and DNA molecules as well as their monomeric units (α, L-amino acids and nucleobases) was tested on bare and Prussian Blue (PB) modified carbon screen printed electrodes (SPE) by cyclic voltammetry and flow injection analysis. In contrast to the generally accepted point of view, the specific electrooxidation of nearly all proteinogenic amino acids, except for Glu, is revealed with constant potential (0.95 V) flow injection analysis on bare carbon SPEs. Furthermore, PB was found to catalyzed this electrooxidation. For 20 amino acids out of 21 tested, the electrogenerated Berlin Green (BG) has been reduced back to PB by amino acids, forming a catalytic cycle that resulted in an enhancement of oxidation signals. The most effective catalysis – the 54-, 31-, and 11-fold current enhancement – was observed for Gln, Ser, and His, respectively. The pronounced catalytic effect of electrogenerated BG on their oxidation has been observed for all proteins tested: human serum albumin, cytochrome *c* from equine heart, and equine skeletal muscle myoglobin. The same catalytic effect of PB was observed toward DNA from herring sperm, oligonucleotides, and nucleobases, while the electrochemical oxidation of guanosine and adenosine 5′-triphosphates has non been enhanced by PB. Presently, PB seems to be the only known material able to catalyze the specific electrochemical oxidation of nearly all protein and DNA molecules under physiological conditions (pH 6.0). Both the increased number of specifically oxidizable proteinogenic amino acids and the achieved efficient electrocatalysis of amino acids and nucleobases oxidation obviously opens new horizons for electrochemical detection of biopolymers (proteins, peptides, DNA, and oligonucleotides).

Acknowledgements:
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K31. Scanning Electrochemical Microscopy Detection of the Hydrogen Peroxide and Hydrogen Generated at Liquid-Liquid Interface

Marcin Opallo,[a] Justyna Jedraszko,[a] Wojciech Nogala,[a] Wojciech Adamiak,[a] Hubert Girault[b]

[a] *Institute of Physical Chemistry PAS, Warsaw, Poland*
[b] *Ecole Polytechnique Federale de Lausanne, Sion, Switzerland*
mopallo@ichf.edu.pl

An interface between two immiscible fluids, like organic and aqueous solutions, belong to the class of so-called soft interfaces. It is macro- and microscopically flat, defect-free and a self-healing. Therefore, it is a perfect platform for catalytic reaction, where reactants (here an electron donor, oxygen and a hydrated proton) are present in separate phases and only meet at the interface. Oxygen and proton reduction are most frequently studied at specific type of liquid-liquid interface: interface between two immiscible electrolyte solution (ITIES). The presence of electrolyte in both phases allows to set potential difference between liquid phases by appropriate selection of electrolytes and their concentration and/or by application of external potential difference to the system. Scanning Electrochemical Microscopy (SECM) is a perfect tool for local detection of the product of two reactions mentioned above: hydrogen peroxide or hydrogen close to the ITIES, especially when concentraion of the product is relatively low.

In the proposed contribution few examples of SECM application to detection of H_2O_2 close to ITIES will be presented. These include oxygen reduction in nonfavourable conditions for proton transfer or in the presence of catalytic (MoS_2) microparticles. We will also demonstrate generation of H_2O_2 when electrolyte is absent in organic phase or when organic phase consists only ions (room temperature ionic liquid). We will present the new method for SECM potentiometric hydrogen detection. Hydrogen was detected by SECM, when electrolyte is organic phase and also when hydrogen generation is driven by light. Finally, we will demonstrate that SECM setup allows for regeneration of electron donor in organic phase.

K32. **Nanoscale Mapping of Chemical and Biochemical Activity at Modified Surfaces**

Agata Roguska,[a] Fatih C. Alcicek,[a] Marcin Holdynski,[a] Magdalena Michalak,[a] Gunther Wittstock,[b] Marcin Opallo,[a] Wojciech Nogala[a]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[b] *Carl von Ossietzky University of Oldenburg, Oldenburg, Germany*
wnogala@ichf.edu.pl

Distribution of active sites at sensing surface influences sensitivity of the sensor. The same concerns heterogeneous catalysts. Therefore, mapping of heterogeneous activity with high resolution is a current interest in characterization of active surfaces. Structure–activity relationships retrieved from activity maps can indicate directions for designing of efficient sensors and catalysts.

Scanning electrochemical microscopy (SECM) is a method for determination of heterogeneous reaction rates and activity mapping. In all analytical modes of SECM the signal registered at the tip depends on both sample activity and tip-to-sample distance. Imaging of activity of samples possessing topographic features is usually performed by recording tip current upon scanning at constant distance above the sample. This requires distance dependent signal, which is independent of variations in activity at the sample. The most common approaches are combinations of SECM with AFM,[1] shear force microscopy,[2] and scanning ion conductance microscopy.[3] These combinations require apparatus extended versus simple SECM and special tip preparation procedures. Moreover, due to common geometric displacement of distance sensing part versus electrochemical probe (parallax), the tip-to-sample distance is not maintained precisely implying inaccuracy in activity mapping. This can be avoided by application of concentric double probes,[3] however, such approach causes difficulties in fabrication of smaller probes for imaging at nanoscale resolution.

In this work we present a method for simultaneous mapping of redox activity and topography with single SECM probe (a nanoelectrode obtained by chemical vapor deposition of carbon inside quartz nanopipette). This method relies on hopping probe in SECM feedback mode without tapping.[4] Maps of local heterogeneous pseudo first order electron transfer rate constant at the sample and its topography are constructed by analysis of tip current-vertical tip displacement relations using developed equations. Proposed method was employed in analysis of regeneration of reversible mediator at a model sample composed of gold nanostructures electrodeposited on indium tin oxide (ITO) support. This method is applicable to nanoscale imaging of activity towards chemically reversible redox processes or processes which stoichiometry allows partial regeneration of the substrate. The latter group comprises disproportionation. Imaging of activity towards disproportionation of hydrogen peroxide by immobilized catalase will be also presented.

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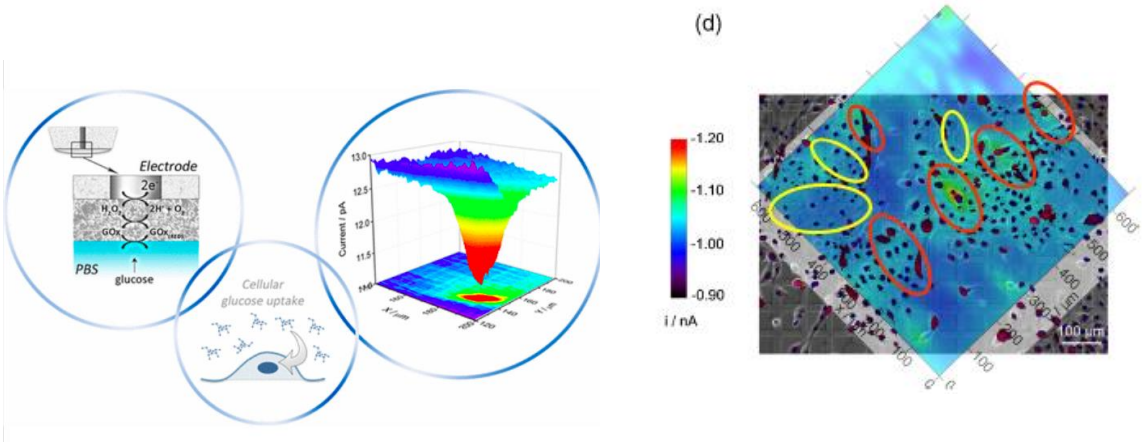
K33. **Functional Imaging of Cellular Processes Using Scanning Electrochemical Microscopy**

Marco Malferrari, Maila Becconi, Simona De Zio, Alice Soldà, Luca Bartolini, Francesco Paolucci, Stefania Rapino

Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, via F. Selmi 2, 40126 Bologna
stefania.rapino3@unibo.it

Cell functional imaging allows identifying cancer cells and helps to elucidate mechanisms of cancer initiation and progression. We use scanning electrochemical microscopy (SECM) as a viable and straightforward technique to detect redox metabolism and redox balance of healthy and cancer cells. We investigated the diagnostic value of SECM images by: (i) tracking oxidized/reduced glutathione (GSSG/GSH) balance to sense oncogenic transformations; (ii) revealing the redox state differences between normal and RasV12 expressing cells and (iii) distinguishing lung carcinoma cells from the surrounding normal epithelium of fresh human biopsies.

It will be shown how to quantify the Warburg effect at single cell level by means of newly developed ultra-microelectrode biosensors and obtain electrochemical imaging of the production of reactive oxygen species. SECM can be used to map in real-time the local concentration and time evolution of key player molecules, such as glucose and lactate, in close proximity of cell membranes and substrates.



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K34. **Molecularly Imprinted Polymers Interfaced with Label-free Transducers: towards Development of Chemosensors for Medical Diagnostics and Environmental Monitoring**

Vitali Syritski

Tallinn University of Technology, Tallinn, Estonia
vitali.syritski@taltech.ee

Despite the considerable progress in modern biosensors, there is a significant limitation mostly related with a labile nature of biological recognition elements, i.e., their poor chemical and thermal stability restricts further development of robust and reusable natural recognition elements. Therefore, the replacement of biological receptors with wholly synthetic analogues has become growing interest. A viable alternative would be materials prepared by the molecular imprinting technique. This technique allows the formation of specific molecular recognition sites in highly reticulated polymeric network grown in the present of analyte molecules, which are subsequently removed leaving behind the analyte specific cavities. The resulting materials, so called, molecularly imprinted polymers (MIPs), endowed with high affinity and selectivity for their target molecules while being more advantageous in terms of mechanical and chemical stability, low cost of preparation and wide range of operating conditions.

This talk will focus on recent advances of our group to develop synthetic receptors based on molecularly imprinted polymers (MIPs) to address the needs of medical diagnostics and environmental monitoring. The study exemplifies the synergistic effect of combining MIP synthetic receptor with various label-free sensing platforms such as surface acoustic wave (SAW),[1-2] surface plasmon resonance (SPR),[3-4] and quartz crystal microbalance (QCM),[5] screen-printed electrode (SPE),[6] and excellent applicability of the resulting sensing systems to affinity measurement and real-time detection of clinically relevant biomarkers and environmental pollutants (Fig.1).

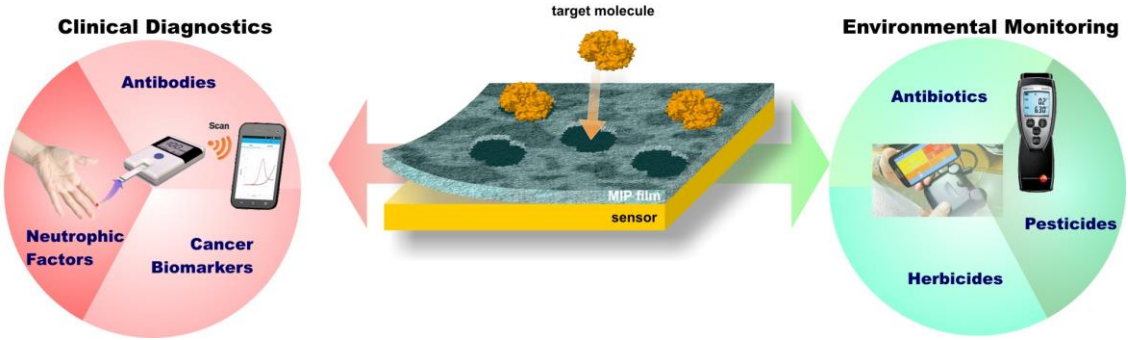

Fig. 1. Concept of MIP-based chemosensors.

Acknowledgment: The Estonian Ministry of Education and Research (grant PRG307).

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SC11. Epitope-MIP for Engineered Enzymes

Aysu Yarman,[a] Giorgio Caserta,[b] Stefan Frielingsdorf,[b] Eszter Supala,[c] Ingo Zebger,[b] Oliver Lenz,[b] Róbert E. Gyurcsányi,[c] Ulla Wollenberger,[a] Frieder W. Scheller[a]

[a] *Universität Potsdam, Institute for Biochemistry and Biology, Potsdam, Germany*
[b] *Technische Universität Berlin, Inst. für Chemie Berlin, Germany*
[c] *Budapest University of Technology and Economics, Budapest, Hungary*
yarman@uni-potsdam.de

In the "classical" synthesis of molecularly imprinted polymers (MIPs) functional monomers and cross-linkers are polymerized in the presence of the target analyte. In the next step, recognition sites are formed by removal of the template. These MIPs have been called plastibodies to stress the analogy of specific binding by antibodies. Whilst antibodies interact only with a small area of its antigen (the immunodeterminant), MIPs typically interact with a large part of the surface of the target molecule. Taking advantage of the simpler MIP synthesis of low-molecular weight molecules short peptide sequences of the C-terminus or N-terminus have been used in the epitope approach. The resulting MIPs have been shown to recognize both the target peptide and the holoprotein. This concept has been extended to peptide tags of engineered proteins, sugars of glycoproteins and even to chemical labels of macromolecules. This approach is closer to the antigen-antibody reaction because only a small exposed part of the macromolecule is recognized by epitope-shaped cavities of the MIP.

Here we present epitope- MIPs for the recognition of engineered proteins carrying the Strep-Tag II, examplified for membrane-bound hydrogenase (MBH) of *Ralstonia eutropha* and alkaline phosphatase. For the MIP synthesis the Cys-extended Strep-Tag II was chemisorbed on the gold electrode prior to electropolymerization of the functional monomer scopoletin. Binding and electrochemical removal of the peptide could be demonstrated electrochemically by using ferricyanide as a redox marker and by Surface-Enhanced Infrared Absorption (SEIRA) spectroscopy. Atomic force microscopy was also applied for monitoring the (different) preparation steps. The redox marker current decreased linearly in the presence of up to 6 nM peptide and reached saturation at 10 nM upon rebinding of the peptide. Moreover, the Strep-tagged proteins, MBH and alkaline phosphatase, were successfully bound to the peptide-imprinted layer. K_D values for Strep-Tag II and MBH to the Strep-Tag II-MIP were calculated to be 3.05 and 33.08 nM respectively, by fitting the binding isotherm to a Langmuir model. Lower K_D values showed that the MIP has a higher affinity than the commercial systems (IBA Life Sciences, Göttingen, Strep-Tag II/Strep-Tactin = 1 µM). Furthermore, the MIP has an almost 10-fold higher affinity to its target than to MBH.

Changing just one amino acid of the peptide significantly reduced its affinity to the MIP. The cross-reactivity tests showed that removal of the terminal tryptophan resulted in an almost 20% lower signal suppression. On the other hand, substitution of a glutamate by the uncharged amino acid glutamine reduced the binding by 75 % which indicates the important role of electrostatic interactions. The dipeptide aspartam had only a very low binding affinity. However, binding of Strep-tagged proteins demonstrated that MIP is highly specific for a group of analytes.

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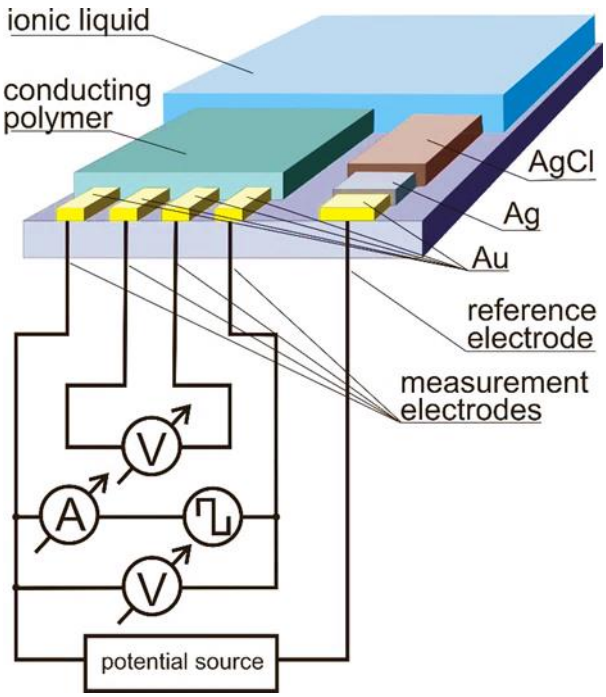
SC12. Electrical Control of the Receptor Affinity

Yulia Efremenko, Vladimir M. Mirsky

Department of Nanobiotechnology, Institute of Biotechnology,
Brandenburgische Technische Universität Cottbus – Senftenberg,
University square 1, 01968 Senftenberg, Germany
efremenk@b-tu.de



A concept of virtual sensor array based on electrically controlled variation of affinity properties of the receptor layer was realized on the base of integrated electrochemical chemotransistor[1-2] containing conducting polymer as the receptor layer. An electrical control of the redox-state of the polymer (polyaniline) was performed in five-electrode configuration with four electrodes for conductivity measurements and Ag/AgCl reference electrode integrated on the same glass chip. Using an ionic liquid was provided electrical connection between the reference electrode and chemosensitive material.[3-4] Conductivity measurements demonstrated potential controlled electrochemical conversions of the receptor material between different redox-states. Binding of trimethylamine at three different potentials, corresponding to these states was studied. The results demonstrated that both kinetic- and equilibrium binding properties of the receptor are controlled by electrical potential thus providing a possibility to form a virtual sensor array using only a single sensing element. The concept was applied for monitoring of fish headspace. Using three characteristics of the sensor response measured at three different redox states of the same sensor material, we have obtained signals from a virtual sensor array consisting of nine chemosensitive elements. The sensor displays systematic changes of its nine signals during fish degradation.[4] This approach can be applied also for the electrical control of affinity of immunoglobulins.[5] A development of a new materials with conducting electrically controlled affinity is in progress. Binding energy of conducting polymers with incorporated a boronic acid functional group was studied by isothermal titration calorimetry, the mostly perspective receptor – ligand combinations were evaluated.

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K35. **Electronic Diversion of Enzymes for Carrying Out Unconventional Tasks**

Emmanuel Suraniti,[b] Aleksandar Karajic,[a,c] Pascal Merzeau,[c] Jérôme Roche,[d] Sébastien Gounel,[c] Andrew G. Mark,[b] Peer Fischer,[b] Nicolas Mano,[c] Alexander Kuhn[a]

[a] *Univ. Bordeaux, CNRS UMR 5255, Bordeaux INP, ENSCBP, 16 avenue Pey-Berland, 33600 Pessac, France*
[b] *Max Planck Institute for Intelligent Systems, Heisenbergstr. 3, 70569 Stuttgart, Germany*
[c] *Centre de Recherche Paul Pascal (CRPP), CNRS UMR 5031, Univ. Bordeaux, 115 Avenue du Docteur Schweitzer, 33600 Pessac, France*
[d] *CIRIMAT, Université de Toulouse, UPS-INP-CNRS, 118 Route de Narbonne, 31062 Toulouse Cedex 09, France*
kuhn@enscbp.fr

Enzymes usually perform the reactions that Nature has made them for. Typically, these thermodynamically favorable schemes transform spontaneously high energy educts into lower energy products. This is related to the fact that (bio)chemical systems do not allow the coupling of energy from several simple reactions to drive a subsequent reaction, which takes place in the same medium and leads to a product with a higher energy than the one released during the first reaction. Normally, the only way to carry out uphill reactions is to use an external input of energy.

Here we present a new approach that shows that it is nevertheless possible to perform such energetically uphill reaction, if the electrons released in an oxidation reaction are temporarily stored in an electromagnetic system, which is then used to raise the electrons' potential energy, so that they can power in a second step, after electrical decoupling, reactions with a higher demand of energy in the same reaction vessel. We exemplify this general concept with a model system based on a glucose/oxygen biofuel cell to drive thermodynamically unfavorable water splitting without input of external energy.[1] Obviously this diversion from the original enzymatic task by electronic means can be also applied to other reaction schemes.[2]

Acknowledgements:
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K36. **Bacterial Biocomposite Materials: a Tool for Optimizing and Studying Extracellular Electron Transfer Reactions**

Mathieu Etienne

Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement, CNRS and Université Lorraine, UMR7564, 405, rue de Vandoeuvre, 54600, Villers-lès-Nancy, France
mathieu.etienne@univ-lorraine.fr

We describe in this work a method to manufacture a biocomposite material by self-assembly of bacteria of the genus *Shewanella oneidensis* MR-1 with carbon nanoparticles in the presence of a protein having a structuring role on the basis of electrostatic interactions. When this material is deposited on the surface of an electrode, it can be used as an electroactive biofilm of artificial nature, in which the structuring protein can then play a role in extracellular electron transfer reactions. In a first step of this study, bovine heart cytochrome *c* was used for the preparation of an artificial electroactive biofilm catalyzing the oxidation of formate. We have shown that the electron transfer was at the redox potential of cytochrome *c*, thus demonstrating the role of this cytochrome in electron transfer reactions between bacteria and nanoparticles. We then sought to catalyze a cathodic reaction, taking as an example the reduction of fumarate. The bovine heart cytochrome *c* no longer allows the electron transfer for this reaction because it has too high a potential, but the bacterial cytochromes of type *c* from the genera *Desulfovibrio* and *Desulfuromonas* have made it possible to demonstrate this catalytic reaction, which demonstrates the great flexibility of this composite material for the electrochemical study of electroactive bacteria. In the two previous examples, the electron transfers were mediated by the exogenous cytochrome introduced artificially into the biocomposite. We then sought to promote direct electron transfer reactions between bacteria and carbonaceous particles by replacing cytochrome c with protamine,[3] which is also known for its structuring role in biological systems. And more recently, we extended this work to electroactive yeast cells.[4] We will discuss the performance of this "living materials" and the potential of this approach for living cell imprinting and electroanalytical applications.

Acknowledgments:
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K37.

Wireless, Battery-less Biosensor Tags Based on Direct Electron Transfer Reactions

Tautgirdas Ruzgas[a,b]

[a] *Department of Biomedical Science, Faculty of Health and Society, Malmö University, 205 06 Malmö, Sweden.*

[b] *Biofilms – research center for biointerfaces, Malmö University, 205 06 Malmö, Sweden*

It is predicted that with the development of Internet-of-Things (IoT) technology by 2025 we expect more than 1000 connected devices per human. One of the key components, which will enable and provide a meaning for such a massive IoT connectivity will be sensors. This includes biosensors. How rapidly and how many biosensors will be integrated into IoT obviously will depend on their cost, robustness, reliability, and simplicity of the design and operation.

Studies of direct electron transfer (DET) between enzymes and electrodes, among other reasons, are aimed to design the simplest and most efficient biosensor designs. In this presentation, the simplicity of the designs of wireless biosensors based on DET will be discussed demonstrating that DET allows construction of wireless biosensors,[1,2] which require no semiconductor elements, Fig. 1. Hopefully, some of such biosensor tags will translate into competitive and useful devices strongly promoting biosensing in IoT networks.

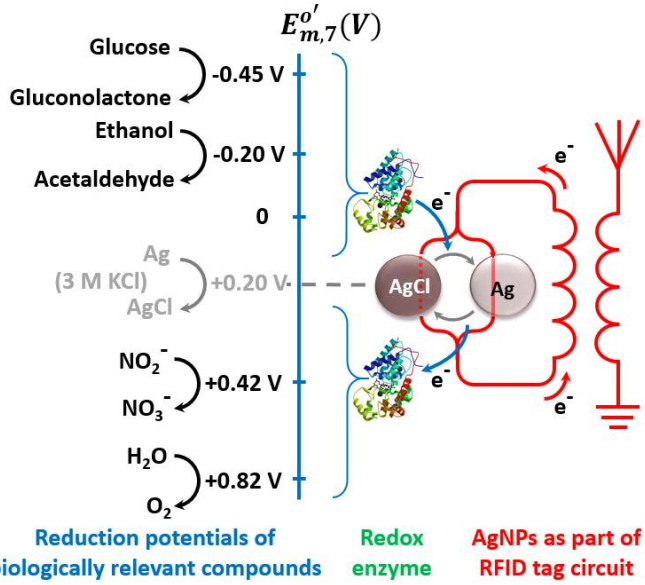

Fig. 1 Illustrates a conceptual representation of battery-less biosensor-RFID (Radio Frequency Identification) tag. AgNPs (silver nanoparticles) constitute a part of RFID tag antenna. An enzyme catalyzes oxidation or reduction of biologically relevant compound converting AgNPs to AgCl or AgCl to metallic AgNPs, respectively. This strongly modulates the impedance of the tag antenna. The tag impedance change is wirelessly monitored as the biosensor response.

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K38. Bioelectrocatalysis and Bioanalytical Applications of Molybdoenzymes

Ulla Wollenberger

University of Potsdam, Institute for Biochemistry and Biology, Liebknechtstrasse 24-25, 14476 Potsdam/Golm, Germany
uwollen@uni-potsdam.de

The phenomenon of bioelectrocatalysis has already been described by Berezin et al more than 30 years ago.[1] Bioelectrocatalysis involves the enhancement of an electrode reaction by a (bio)catalytic process and allows therefore to gain important kinetic information about the catalyst. The presence of the catalyst enables redox reactions of compounds at electrode to occur at low overpotentials and together with the substrate selectivity bioelectrocatalysis provides the basis for sensitive and selective electroanalytical devices. The signal transduction between the catalyst protein and redox electrodes proceeds by direct electronic communication and by mobile or polymer bound redox mediators. Recent progress in the field is due to advances in enzyme engineering, surface chemistry and nanotechnology.

In this talk examples of electrochemical studies on molybdenum containing enzymes and biosensors based on them will be discussed. Molybdenum containing enzymes catalyze important metabolic conversions such as oxidation of aldehydes, xanthine, and sulfite, or the reduction of DMSO, CO2 and nitrate.[2] More than 50 molybdoenzymes were identified to date. These enzymes have a complex overall architecture and generally contain multiple redox-active centers to transduce between the two-electron redox reaction of the substrate at molybdenum cofactor (Moco) and the terminal electron donor/ acceptor site. Strategies to immobilize protein and enzymes based on self assembled monolayers, detergents and three dimensional sensor structures were successfully developed in order to achieve an efficient electronic communication between enzyme and electrode and a high catalyst loading particular for direct electron transfer and mediatorless bioelectrocatalysis. On the other hand immobilization is achieved in redox polymers for mediated electron transfer. The lecture will discuss examples of such electrochemical biosensors, i.e. electrodes for aromatic aldehydes with an aldehyde oxidoreductase,[3,4] for sulfite with sulfite oxidase on nanoparticle modified electrodes,[5-7] and a sensor for N-methylamine oxides with an enzyme of the class of DMSO reductases.[8]

Acknowledgments:
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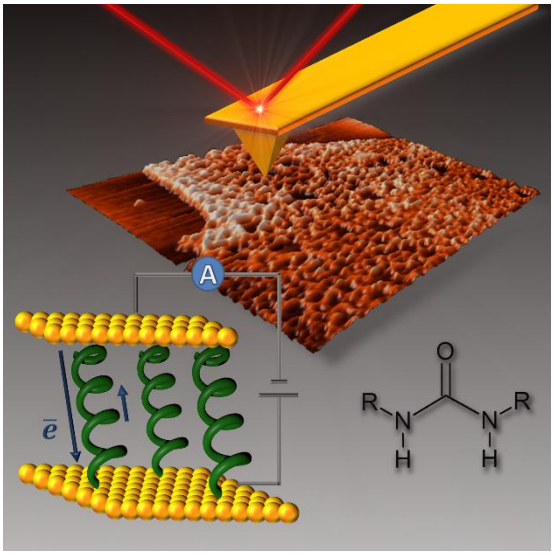
K39. **Electron Transport in Nanoscale Junctions with Helicomimetic Foldamers**

Sławomir Sęk,[a] Karolina Pułka-Ziach,[b] Joanna Juhaniewicz-Dębińska,[a] Anna Puszko[b]

[a] *Faculty of Chemistry, Biological & Chemical Research Centre, University of Warsaw, Warsaw, Poland*
[b] *Faculty of Chemistry, University of Warsaw, Warsaw, Poland*
slasek@chem.uw.edu.pl

Electron transport in proteins and peptides is crucial for energy conversion in biological processes like photosynthesis, respiration and enzymatic reactions. Therefore, the important goal of the fundamental research is to provide insight into the mechanisms determining peptide-mediated electron transport. Peptides are known to adopt variability of structural motifs and when suitably designed, they can also serve as components of biosensing devices or nanoscale bioelectronic circuits. In this area of research, significant progress has been made due to the development of experimental methods, which enable fabrication of nanoscale junctions with peptide monolayers bridging two conductive electrodes. Among them, scanning probe microscopy (SPM) offers unique capability to investigate electric properties of individual molecules or molecular films.[1] Such approach involves entrapment of the assemblies of molecules between two metallic contacts established by metal support and conductive probe of SPM. When the bias voltage is applied between the contacts, the resulting current flow depends on the properties and structural features of peptide molecules forming the assembly including their length, secondary structure, dipole moment, the nature of the constituent amino acids or charge. Importantly, SPM-based method enables control of the mechanical strain or stress of the molecular film incorporated into the junction.[2]

Among variety of structural motifs, α-helical peptides were proved to be efficient mediators of electron transport. However, their use is limited to compounds containing at least 8 amino acid residues. To overcome this problem, we have designed molecular junctions utilizing α-helicomimetic foldamers based on oligourea backbone. These particular compounds possess important features: (a) it is possible to synthesize oligoureas containing side chains of all natural amino acids; (b) the folding process of oligomers is not affected by the nature of side chains. Such characteristics make them highly robust, tunable and hence useful in the studies of electron transport processes. Additionally, only four acyclic residues are sufficient to drive complete helical turn formation. We have demonstrated that oligoureas may act as efficient electron transport mediators and the oligourea helix is more stable than the helix formed by peptides. Interestingly, electron transmission through longer analogs shows strong directional dependence, which is characteristic for diode-like behavior.[3,4]



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SC13. **Simple Methods for the Electrified Liquid – Liquid Interface Downscaling. From Design to Sensing Applications**

Lukasz Poltorak,[a,b] Konrad Rudnicki,[a] Irene Eggink,[b] Marnix Hoitink,[b] Slawomira Skrzypek,[a] Ernst J. R. Sudhölter,[b] Marcel de Puit[b,c]

[a] *Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, University of Lodz, Tamka 12, 91-403 Lodz, Poland*
[b] *Delft University of Technology, Department of Chemical Engineering, Van der Maasweg 9, 2629 HZ Delft, The Netherlands*
[c] *Netherlands Forensic Institute, The Hague, The Netherlands*
lukasz.poltorak@chemia.uni.lodz.pl

Electrochemistry knows the liquid – liquid interface as the interface between two immiscible electrolyte solutions (ITIES) or electrified or polarized soft junction. On its own, it has a number of inherent and unique properties. It is self-healing and renewable, can be polarized in a purely ionic manner and allows the study of the interfacial charge transfer reactions. For the latter, associated currents can be recorded in a form of interfacial electrons and/or ions transfer. The interfacial modification is a topic on its own. The interface can receive new properties after being decoration with a smart nano-objects, molecular self-assemblies or by placing it in an appropriate support.[1]

The flowing nature of the immiscible liquids used to create the ITIES helps when it comes to interface miniaturization. This is usually performed in a relatively easy manner with patterned membranes, micro- or nano-capillaries used as a support. In this respect, the secret is to adjust the chemical properties of the interior of voids and/or pores within the support so that only one of the liquids will be in favor to wet their surface. Addition of the second, immiscible phase results in the formation of a miniaturized liquid – liquid interface bringing a few qualities to the investigated system: (i) ITIES receives additional stability; (ii) downscaling facilities interfacial modification process; whereas from the electroanalytical point of view (iii) lower capacitance currents can be translated into lower detectable concentration of analyzed species and (iv) establishment of the hemispherical diffusion zones improves the analyte mass transport towards the interface, which results in a higher detection sensitivity.

In this work, I will present two very simple methods used to prepare a micro-capillaries which are subsequently used as a support for the ITIES. First method, is based on a metal microwire (DIA = 25 µm) entrapped and dissolved from a glass framework.[2] In the second approach, we used the fused silica capillaries (DIA equal to 5; 10 and 25 µm) that are sliced and embedded in a heat shrinking tube.[3] Resulting devices are then used as the sensors for cocaine determination from a real street samples[1-4] or to perform electroanalytical screen the family of fluoroquinolone antibiotics.[5] The fabrication process, comprehensive electroanalytical description and further challenges will be presented and discussed.

Acknowledgments:
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K40. Single-cell Nanoencapsulation

Insung S. Choi

Center for Cell-Encapsulation Research, Department of Chemistry, KAIST, Korea
ischoi@kaist.ac.kr

Nature has developed a fascinating strategy of cryptobiosis for counteracting the stressful, and often lethal, environmental conditions. For example, certain bacteria sporulate to transform from a metabolically active, vegetative state to an ametabolic endospore state. The bacterial endospores, encased within tough biomolecular shells, withstand the extremes of harmful stressors, such as radiation, desiccation, and malnutrition, for extended periods of time and return to a vegetative state by breaking their protective shells apart when their environment becomes hospitable for living. Inspired by cryptobiosis found in nature, researchers have sought to chemically control and tailor the metabolic behaviors of non-spore-forming cells as well as enhancing their viability against adverse environmental conditions, by forming thin (< 100 nm), tough artificial shells. These living "cell-in-shell" structures, called artificial spores, enable chemical control of cell division, protection against physical and chemical stresses, and cell-surface functionalizability, armed with exogenous properties that are not innate to the cells but are introduced chemically. The field has further advanced to the stage of chemical sporulation and germination, where cytoprotective shells are formed on living cells and broken apart on demand. The (degradable) cell-in-shell hybrids are anticipated to find their applications in various biomedical and bionanotechnological areas, such as tissue engineering, cytotherapeutics, high-throughput screening, sensors, and biocatalysis, as well as providing a versatile research platform for single-cell biology.

K41.

2D and 3D Lab-on-a-Chip Systems for Life Science Applications

Jenny Emnéus

DTU Bioengineering Kgs. Lyngby, Denmark
jemn@ dtu.dk

The clinical need for functional replacement of tissues and physiologically relevant drug screening models has fuelled research into engineering in-vitro tissues. In conventional 2D cell cultures, cells tend to loose key specific functions that they normally exhibit due to the absence of complex cell-cell, cell–matrix and cell factor interactions that are usually present in vivo. The trend thus goes towards culturing cells in a 3D environment. While cells in vivo are typically no further than 200 µm away from the nearest blood vessel, enabling their nutrient requirements to be met through diffusion of the necessary chemical species, the absence of functional vasculature in tissue engineered constructs poses a significant challenge when attempting to grow tissues of clinically relevant sizes. An enhanced mechanism for transport of oxygen and nutrients is required with a growing trend of using porous scaffolds to guide cell assembly into 3D constructs for engineering different types of tissues. Moreover, depending on the tissue of interest, the scaffold stiffness (Youngs/elastic modulus) is a vital consideration and varies from tissue to tissue (e.g. Brain 0.1-16 kPa, Liver 5-10 kPa, bone 15-30GPa).

The human population is getting increasingly older. Hence, age-related neurodegenerative diseases like Parkinson's disease (PD) are imposing an escalating threat as a medical, economical, and emotional burden. For decades, PD has been studied in animal and simple cellular models. While in many aspects these models are irreplaceable, they are inherently limited in others. Low success of clinical trials for new drugs and therapies has recently turned attention to poor translation of animal experiments to human outcomes. On the other hand, simple cell cultures lack *in vivo* tissue complexity. Therefore, a need for a more advanced human *in vitro* models has emerged. 2D and 3D electrochemical Lab-on-a-Chip (LOC) systems will be presented that can be applied in organ-on-a-chip applications. 2D chips are equipped with a planar electrode array explored for intra and extracellular events using voltammetric and/or impedimetric detection. 3D systems are equipped with different scaffolds for support and culturing of cells, having: (a) Structured perfusable channel network, enabling delivery of necessary nutrients and oxygen to the interior of the scaffolds. (b) Secondary more arbitrary random porous network that can enclose a hydrogel phase with a "nearby" source of important cell factors, supporting the growth and differentiation of cells. (c) Multiple functions, as a cell carrier and as combined optical waveguide and electrical sensor for e.g. optogenetic applications. Examples of 2D and 3D systems applied in relation to drug delivery, as potential brain implants exemplified for Parkinson´s disease will be presented.

The applicability of the presented systems spans from enzyme/antibody based biosensor array systems for environmental and diagnostic biomedical bioanalysis to cell- and organ on chip system for better *in vivo* mimicking toxicity or drug screening.

SC14.

Protein imprinting. Better control over deposited polymer structure for better sensor performance.

Maciej Cieplak,[a] Marcin Dąbrowski,[a] Jakub Kałęcki,[a] Agnieszka Zimińska,[a] Krzysztof Noworyta,[a] Alexander Kuhn,[b,c] and Piyush Sindhu Sharma [a]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS), Kasprzaka 44/52, 01-224 Warsaw, Poland*

[b] *Institut des Sciences Moléculaires, University of Bordeaux, Bordeaux INP, ENSCBP, 16 Avenue Pey Berland, 33607, Pessac, France*

[c] *CNRS, ISM, UMR 5255, 351 Cours de la Liberation, 33400, Talence, France*

mcieplak@ichf.edu.pl

Protein imprinting is a challenging task mainly because of their large size. It is very difficult to estimate which and how many groups on the protein template molecule surface are accessible for binding. To overcome this drawback, we introduced semi-covalent protein imprinting. We prepared a conducting molecularly imprinted polymer (MIP) based on bis(2,2′-bithien-5-yl)methane for human serum albumin (HSA) determination. A very high imprinting factor (IF > 20) and selectivity of the devised chemosensor proved that we the MIP featured molecular cavities of well-defined structure and high affinity to HSA. This success encouraged us to improve this approach even further. For that, we prepared a macroporous MIP film with hierarchical nanostructure controlled at three different size scale levels. Introduction of this nanostructure resulted in extraordinary properties of this recognizing material. Very high selectivity of MIP sensor was accompanied by sensitivity and detectability at an impressive femtomolar concentration level. To prove versatility of this approach we also prepared macroporous MIP sensors for more demanding target proteins, namely, human chorionic gonadotropin (hCG) and follicle-stimulating hormone (FSH).

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SC15. **Towards SERS-based Detection of DNA Mutations**

Aleksandra Jaworska,[a] Edyta Pyrak,[a,b] Andrzej Kudelski[a]

[a] *Faculty of Chemistry, University of Warsaw, ul. Pasteura 1, 02-093 Warsaw, Poland*
[b] *Nencki Institute of Experimental Biology of Polish Academy of Sciences, Warsaw, Poland*
jaworska.aleksandra.maria@gmail.com

Early diagnosis of cancer early is vital to successful treatment. Unfortunately, many malignancies are detected at a stage of progression beyond when surgical resection or other interventions can be effectively implemented. New detection tools are therefore needed that overcome the poor levels of detection and/or high costs symptomatic of many of the approaches in use today. Surface-enhanced Raman spectroscopy (SERS) is a very sensitive and powerful tool for molecular detection upon adsorption on gold and silver nanoparticles (colloids, electrodes and other surfaces).[1] It relies on the plasmonically amplified electric fields that are excited upon irradiation of with optically resonant light. This amplification enhances the electric field within a few nanometers of the particle surface, magnifying a normally weak Raman signal by a factor of 10^6 and enabling the trace level detection of a wide range of compounds. Because of its high sensitivity and low limit of detection, SERS can be successfully applied for biological purposes as an alternative for routinely used PCR. SERS biosensors with the use of labels are based on high cross section on Raman scattering of certain organic molecules called Raman reporters/nanoprobes (especially dyes). The idea of a sensor, shown in Figure 1, is quite simple. Briefly, single stranded DNA (ssDNA1 in Figure 1) is immobilized on a metal surface forming a monolayer, and then a small amount of sample is placed on this structure. Together with ssDNA it forms dsDNA during the hybridization process, and then it can be covered by another layer of ssDNA (ssDNA2) labelled with Raman reporter molecules enabling recording SERS signal.[2] In this presentation, I will present the different experimental procedures for preparation of SERS – based sensors as a potential tool for detection of DNA mutations.

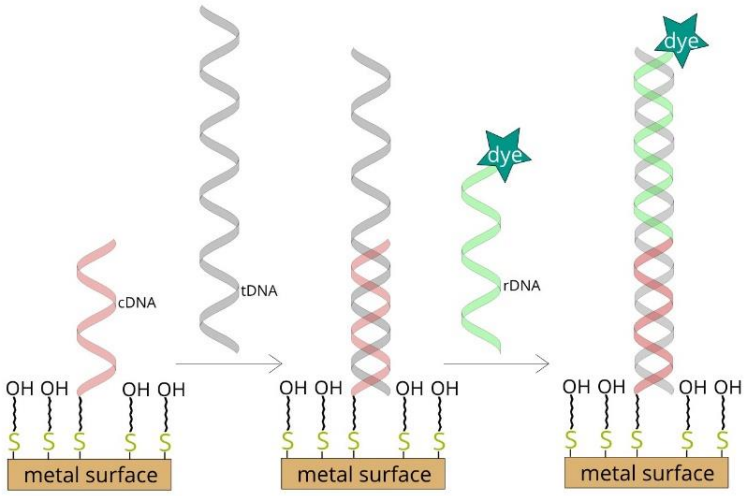

Figure 1. Scheme of typical SERS – based nanosensors for DNA detection.

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SC16. About Gold Nanotriangles and Their Applications

Lidia J. Opuchlik,[a] Olga A. Swiech,[a] Michal Kizling,[b] Renata Bilewicz,[a]

[a] *Faculty of Chemistry, University of Warsaw, Ludwika Pasteura 1, Warsaw, Poland*
[b] *College of Inter-Faculty Individual Studies in Mathematic and Natural Sciences (MISMaP), Stefana Banacha 2C, Warsaw, Poland*
lgoralska@chem.uw.edu.pl

Current cancer research is aimed to develop new anticancer therapies as well as to improve the performance of already discovered ones. We synthesized two types (pH-sensitive and pH-insensitive) of anisotropic nanotriangles (AuNTs) as carriers for doxorubicin.[1] Due to atypical optical properties resulting from triangular shape, these drug-carrier conjugates are sensitive to light in the near-IR region (in which human tissues do not absorb) and can induce hyperthermic cytotoxicity (convert light energy to heat). Also, their optical properties make them suitable for medical imaging and detection. Therefore, they are very interesting because they can be considered as multifunctional therapy agents – not only efficient drug carriers but also thermal energy generating agents. We performed detailed studies of prepared conjugates. The optical properties, shape and size were evaluated by UV-vis-NIR spectroscopy, SEM and DLS. Fluorescence studies demonstrated different drug release profiles depending on the pH. MTT assay performed on two cell lines (A549 and HeLa) revealed that gold nanostructures modified with doxorubicin were more toxic than free doxorubicin. Viability tests and confocal microscopy revealed that the bond between the gold carrier and the drug determined the pathway of cell death – apoptotic in the case of peptide bonding and sudden and necrotic when a hydrazone linker was employed.

Another application of gold nanotriangles results from their interesting structural features – multiple edges and structural defects remaining after synthesis by wet-chemistry – granting them good catalytic activity. These novel-shaped nanoparticles may be used as effective means for modification of working electrodes exhibiting multiple edges or curvature effects, all possessing roughened surface area. Therefore, they can be utilized as supports in catalysis. Glassy carbon electrode coated with AuNTs was used for the study of oxygen reduction reaction (ORR) in 0.5 M sulfuric acid.[2] The applied activation procedure led to a surface highly active towards oxygen reduction. The advantages: much lower overpotential and larger current densities of oxygen reduction are ascribed to the unique nanostructures present on the carbon electrode surface – the gold nanoplates which are rich in edges providing a large population of Au (100) sites with unsaturated coordination exposed to the solution, and catalytically active. Measurements performed using a rotating disc electrode, modified with the gold nanoplates, confirmed that ORR proceeds via two separate steps: oxygen is reduced to hydrogen peroxide, and the peroxide is further reduced in a two-electron reduction to water.

Currently we are working on multicomponent polymers doped with nanotriangles modified with cyclodextrin derivatives. Such systems can be utilized in electrochemical sensors or in (bio)electrocatalysis. The use of cyclodextrin derivatives provides selectivity and enhances binding of analytes. The introduction of AuNTs, evenly dispersed in the polymer matrix, provides the enhancement of the signal due to the significant increase of the conductivity of the fabricated material. Additionally, the use of easily-wettable short oligoethylene glycol for crosslinking and structuring allows binding of the analyte in the whole volume of the polymer thanks to the uninterrupted diffusion within the material.

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Tuesday, November 12

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: A. Kuhn / L. Opuchlik
09:00-09:40	T05	**Sergey Shleev** Non-invasive Electrochemical (Bio)sensors Operating in Human Physiological Fluids
09:40-10:00	K42	**Hanna Radecka** Ultrasensitive Electrochemical Sensors for Exploring of Anion Recognition Processes at Aqueous/Solid Interface
10:00-10:15	SC17	**Nabila Yasmeen** Electropolymerized Molecularly Imprinted Polymer towards Chemosensing of an Autism Biomarker
10:15-10:30	SC18	**Luís C. Almeida** Electrosynthesized Poly(catecholamine) Films Modified with Ethanolamine for Immunosensing
10:30-11:00		**Coffee break**
11:00-12:00		**Morning session 2** Chairs: S. Shleev / Y. Efremenko
11:00-11:20	K43	**Lo Gorton** Connecting Biological Membranes and Bacterial Cells to Electrodes through Redox Polymers
11:20-11:35	SC19	**Kamila Łępicka** The poly[NBI-(DTP)2] as an electrode material for the inherently asymmetric supercapacitor
11:35-11:50		Closing
12:00-13:00		**Lunch**
13:30-		**Departures**

T05. Non-invasive Electrochemical (Bio)sensors Operating in Human Physiological Fluids

Sergey Shleev, Stefan Cirovic, Magnus Falk

Department of Biomedical Science, Faculty of Health and Society, Malmö University, Malmö, Sweden
sergey.shleev@mau.se

A significant effort is being devoted into the development of new healthcare and fitness innovations, driven by the need imposed by patients and individuals, as well as the possibilities provided by recent electronics, especially combined with information technology, to evaluate and benchmark personal health parameters.[1-3] By designing non-invasive (bio)sensors operating in human physiological fluids, such as sweat, urine, saliva, and lachrymal liquid, it is possible to perform continuous, non-invasive monitoring of biomarkers for assessing human performance, health and wellbeing.[4] Such new technologies enable a shift from professional medical care provided by hospitals to essentially outsourced medical services at point-of-care units and homes and individuals being able to self-assess, to a much lower cost than what is currently possible.[5]

The keynote lecture will overview recent progress in the development of non-invasive biosensors operating *ex vivo*.[6-9] However, it will be mostly focused on electrochemical devices, which have been designed and tested at the Department of Biomedical Science, Malmö University, Sweden. Specifically, the following electrochemical (bio)sensors will be discussed: (*i*) flexible micro(bio)sensors for quantitative analysis of bioanalytes in a nanovolume of human lachrymal liquid [10], (*ii*) wireless biosensing systems for glucose and lactate monitoring in human urine, and (*iii*) headphone based electronic tongues for direct continuous sweat analysis (Figure 1).

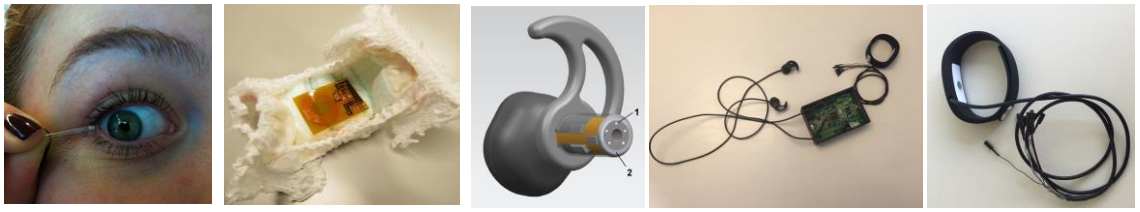

Figure 1. Electrochemical (bio)sensors developed at the Department of Biomedical Science.

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K42. **Ultrasensitive Electrochemical Sensors for Exploring of Anion Recognition Processes at Aqueous/Solid Interface**

Hanna Radecka, Jerzy Radecki

Institute of Animal Reproduction and Food Research, Polish Academy of Sciences, Tuwima 10, 10-748 Olsztyn, Poland

In recent decade, the intermolecular recognition of anions in water has been attracted the attention of numerous scientific groups involved in supramolecular chemistry.[1,2] The most of literature reports the recognition of anions in one organic phase. Developing systems for the recognition of anions in water medium is still a challenging task. The several analytical approaches for anion recognition at aqueous/solid interface based on the following redox active monolayers deposited on the gold electrodes will be presented: (i) dipyrromethene –M(II)- dipyrromethene- dipodal anion receptor,[3] (ii) terpirydyne–M(II)-dipyrromethene- dipodal anion receptor, (iii) dipyrromethene –M(II)- dipyrromethene- cyclopeptide[4] [M(II)= Cu(II) and Co(II)].

The developed systems were characterized electrochemically using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV). Then, they were successfully applied for the electrochemical recognition of anions (Cl^- and SO_4^{2-}) in highly diluted aqueous medium (in the picomolar range). The mechanism of communication between the redox centre and receptor anion complex as well as analytical signal generation will be discussed.

Acknowledgements:
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SC17. Electropolymerized Molecularly Imprinted Polymer towards Chemosensing of an Autism Biomarker

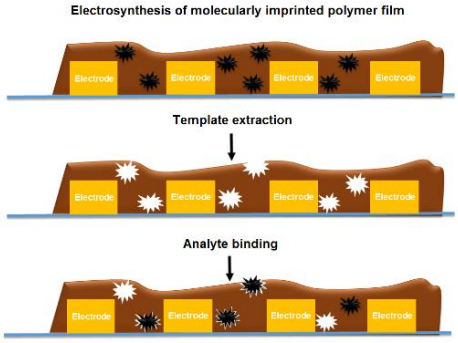
Nabila Yasmeen,[a] Piyush S. Sharma,[a] Mathieu Etienne,[b]
Francis D'Souza,[c] Wlodzimierz Kutner,[a,d]

[a] *Institute of Physical Chemistry, Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Laboratory of Physical Chemistry and Microbiology for Materials and the Environment,54600 Villers-lès-Nancy, France*
[c] *Department of Chemistry, University of North Texas, Denton, 1155, Union Circle, #305070 TX 76203-5017, USA*
[d] *Department of Mathematics and Natural Sciences, School of Science, Cardinal Stefan Wyszynski University, Warsaw, Poland*
nyasmeen@ichf.edu.pl

Nowadays, molecularly imprinted polymers (MIPs) are widely used as substitues for biologically derived antibody-antigen systems for determination of different analytes of interest, such as biocompounds, metabolites, and even whole bacteria because of their high affinity, sensitivity and durability under harsh environmental conditions.[1-3] Several biocompounds including gamma aminobutyric acid (GABA) is reported as autism spectrum disorder (ASD) biomarkers.[4,5] Therefore, there is an urgence to devise chemosensor for selective and sensitive determination of the GABA biomarker of ASD.

In the present study, we deposited an MIP film on the interdigitated array (IDA) electrodes by electropolymerization for fabrication of a chemosensor of ASD biomarkers. The IDA electrodes are particularly attractive because their geometric features differences from those of conventional electrodes resulting in different electrochemical behavior. This includes semi-spherical diffusion to each micro band, fast establishment of a steady-state mass transfer, small iR drop, high redox cycling along with the high signal-to-noise ratio within a dynamic range of potential.[6,7] These all features make electrochemical measurements on IDA electrodes highly sensitive for analytes at a considerably low detection limits.

For designing of selective molecular cavities in the MIP, *bis*-bithiophene derivatized functional monomers were used. The impedance based transduction determined GABA in the micromolar concentration range. This high detectability indicates chemosensor potential suitability in clinical analysis applications.



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SC18. **Electrosynthesized Poly(catecholamine) Films Modified with Ethanolamine for Immunosensing**

Luís C. Almeida,[a] Tânia Frade,[a] Rui D. Correia,[a] Yu Niu,[b] Gang Jin,[b] Jorge P. Correia,[a] Ana S. Viana[a]

[a] *Centro de Química e Bioquímica, Centro de Química Estrutural, Faculdade de Ciências da Universidade de Lisboa, Lisboa, Portugal*
[b] *NML, Institute of Mechanics, Chinese Academy of Sciences, Beijing, China*
lmalmeida@fc.ul.pt

Polydopamine-based surface modifications have been widely studied to obtain biocompatible and versatile materials for biomedical, energy and industrial applications.[1] The spontaneous oxidative polymerization in aerated mediums makes it a simple and almost universal method for material coating, enriching the substrate with quinone groups available for further functionalization by Michael-type addition or Schiff-base formation.[2] In fact, a robust immobilization of biomolecules, that allows the retention of its biological activity, is a desired feature of the supporting matrix in a biosensors.[3] Nonetheless, the control over structural organization, homogeneity, oxidation state and conductivity of polydopamine thin films is still difficult to achieve, limiting the technological application of this material. Besides oxygen, other chemical oxidants,[4] have been used to increase polymerization rate, obtaining different porosities and chemical structures. More recently, electrosynthesis has shown to yield better electrochemical transducers in biosensing interfaces than the standard chemical synthesis,[5] highlighting the great potential of electrochemical methods to better tune the chemical and physical properties of poly(catecholamines).

Hereby, we report a comprehensive study of the electropolymerization of distinct catecholamine monomers (dopamine, norepinephrine and L-DOPA), showing novel insights of the underlying mechanism supported by electrogravimetric data. The precise control over the growth charge, mass and optical thickness allows the synthesis of poly(catecholamine) films with different chemical composition, redox properties, ionic permeability, wettability and morphology. Real-time Surface Plasmon Resonance assays are conducted to assess the adsorption of different proteins to the biomimetic films. Furthermore, the ability to inhibit the non-specific adsorption is achieved by one-step or two-steps modifications of the polymers with ethanolamine. The antigen-antibody specific interaction was evaluated using immunoglobulin G and its respective antigen, as model proteins. The powerful combination of several surface characterization techniques allowed to demonstrate the very promising applications of poly(catecholamine) films in immunosensors as controllable, reproducible and versatile biorecognition layers.

Acknowledgments:
This work was funded by Fundação para a Ciência e a Tecnologia through PhD scholarship SFRH/BD/129566/2017 and projects: IF/00808/2013/CP1159/CT0003 (POPH, UE-FSE), UID/MULTI/00612/2019 and PTDC/CTM-NAN/0994/2014.

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K43. Connecting Biological Membranes and Bacterial Cells to Electrodes through Redox Polymers

Lo Gorton

Department of Biochemistry,
P.O.Box 124, SE-22100 Lund University, Lund, Sweden
Lo.Gorton@biochemistry.lu.se

We have throughout the years since 2004 pioneered "wiring" both Gram-positive and Gram-negative bacteria[1-4] (and thylakoid membranes[5-7]) to electrodes using osmium redox polymers (Os RPs) that will strongly facilitate extracellular electron transfer (EET). Because of the cationic nature of the Os RPs they will electrostatically interact very strongly with membranes and cells to form hydrogels that will strongly attach on electrode surfaces and will allow substrates and products to freely diffuse in and out of the hydrogel. We have investigated the influence of E°'-value and structure of the Os-complexes of the Os RPs on the rate of electron transfer. However, only recently we have obtained a much more clear picture on how the RPs and the cells interact and how the interaction changes with time. In these recent investigations we have "wired" wild type and some mutants of *Enterococcus faecalis* with both 4 different Os RPs as well as with a quinone RP.[8-11] These recent results will be shown and discussed.

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SC19. The poly[NBI-(DTP)$_2$] as an electrode material for the inherently asymmetric supercapacitor

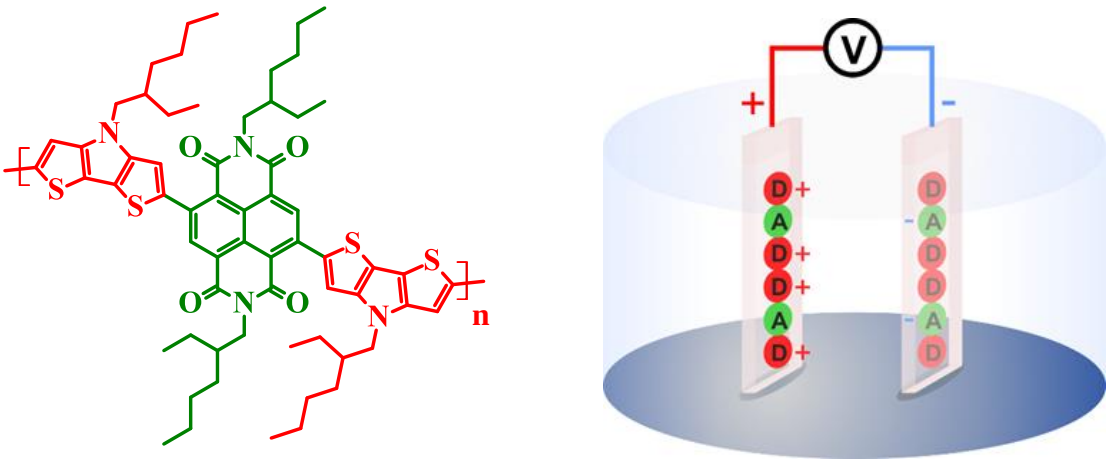
Kamila Łępicka,[a] Renata Rybakiewicz,[b] Piotr Pieta,[a] and Wlodzimierz Kutner [a,b]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Faculty of Mathematics and Natural Sciences, School of Sciences, Cardinal Stefan Wyszynski University in Warsaw, Wóycickiego 1/3, 01-815 Warsaw, Poland*
klepicka@ichf.edu.pl

The current interest in fabrication of polymers suitable for application as electroactive materials for electrodes of electrochemical capacitors, also known as supercapacitors (SCs), is mainly focused on conducting polymers with limited operating voltage. An ambipolar SC electrode material provides conductivity extending over a very wide voltage range. This property is highly desirable for devising and fabricating novel energy storage materials with high capacity and energy density. Conducting ambipolar polymers are polymers electroactive in both the negative and positive potential range. This unique feature introduces the desired high both operation voltage to the SC device. Favorable structures of ambipolar polymers containing conducting donor units, conjugated with conducting acceptor units, are responsible for enhanced charge conduction in a broad potential range. Hence, they are very promising for preparation of high-performance SCs in terms of high energy density and power density.

In the present research, the poly[NBI-(DTP)$_2$] (Scheme 1a) film was utilized to fabricate a laboratory model of a new inherently asymmetric SC (Scheme 1b). The fabricated device exhibited a very broad working voltage range of 2.0 V in the 0.1 M (TBA)PF_6 solution of propylene carbonate, delivering a high energy density of 47 Wh kg^{-1} at the power density of 1342 W kg^{-1}. Moreover, electrodes made of poly[NBI-(DTP)$_2$] are electrochromic. Therefore, they can serve as an internal charging−discharging indicator in this SC.

a b



Scheme 1. (a) The structural formula of poly[NBI-(DTP)$_2$] where the naphthalene bisimide (NBI) acceptor (A) moiety is symmetrically core functionalized with two dithienopyrrole (DTP) donor (D) moieties. (b) The supercapacitor constructed from two Au electrodes coated with poly[NBI-(DTP)$_2$] films.

Poster Session

Saturday, November 9
20:00-22:00

P01. Characterization of Molecularly Imprinted Polymer Fixed Electrode Surface by MIP-Nanoparticle

Masaki Abe,[a] Haruto Eguchi,[a] Akihiko Hatano,[b] Yasuo Yoshimi[a]

[a] *Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan*
[b] *Shibaura Institute of Technology, 307 Fukasaku Minuma-ku, Saitama 337-8570, Japan*
yosimi@sic.shibaura-it.ac.jp

A molecularly imprinted polymer (MIP) is molecular-recognition material synthesized by polymerization in the presence of the target molecule as a template. We are developing highly selective electrochemical sensors for vancomycin (VCM), which is one of the primary antibacterials, by using VCM-imprinted (methacrylic acid (MAA)-co-methylenebisacrylamide (MBAA)-co-acrylamide-co-ferrocenyl monomer) on an electrode.[1] The ferrocenyl monomer (vinyl ferrocene (VF) or allylaminocarboxypropyonic-3-ferrocene (ACPF)) is essential for the VCM sensing but the role is still unknown. We also discovered that nanoparticle of MIP (MIP-NP) is swelled by the specific interaction with the template.[2] In this work , we analyzed the size dependency of the MIP-NP of VCM composed by the same material as the MIP on the electrode in order to discuss the role of the ferrocenyl group.

VCM was immobilized covalently on the aminated surface of glass beads via glutaraldehyde. MIP-NP was synthesized at the surface of glass beads by radical copolymerization of MAA, MBAA and ferrocenyl monomer (VF, ACPF, or none). MIP-NP was obtained by washing glass beads surface phosphate buffer saline including 1.0 M NaCl. The particle diameter was measured by dynamic scattering spectroscopy (DLS).

The diameter MIP-NP containing ACPF is larger than that containing VF or that without ferrocenyl group. The VCM-MIP electrode containing ACPF was more sensitive to VCM that that containing VF or no ferrocenyl monomer. The consistency indicates that the ferrocenyl group of ACPF has strong affinity with VCM.

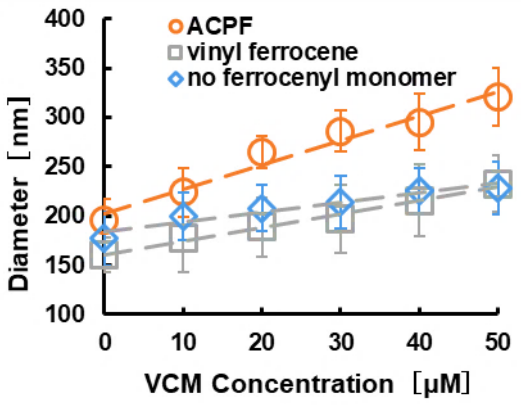


Fig. 1 Size dependency of the MIP-NP

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P02. A Self-powered Glucose Sensor with Optical Readout

Jana M. Becker, Tim Bobrowski, Felipe Conzuelo, Adrian Ruff, Wolfgang Schuhmann

Analytical Chemistry - Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr University Bochum, D-44780 Bochum, Germany
Jana.Becker@rub.de

Glucose has a critical role as main energy source for living organisms. Metabolic disorders, like diabetes, where the glucose level in the body is disturbed, have vast impacts for the people affected. Hence, easy-to-apply point-of-care devices, which allow on-site monitoring of the glucose level in the blood are highly desired. Therefore, substantial efforts have been made to create miniaturized low-cost point-of-care devices,[1] which can be handled by the patients themselves.

In this context, we report the fabrication of a self-powered glucose sensor, which possesses an optical transducer for simple and fast optical readout with the bare eye. The sensing device consists of a glucose-powered biofuel cell compartment and a PEDOT based electrochromic reporter for optical readout, both immobilized on a single screen-printed electrode chip (Figure 1a). A glucose/O_2 biofuel cell is used, in which glucose is oxidized to glucono-δ-lactone by the oxygen-insensitive enzyme PQQ-GDH, which is wired to the electrode by the low potential redox polymer poly(1-vinylimidazole-*co*-allylamine)-[Os(dmxy-bpy)$_2$Cl]Cl. O_2 reduction to H_2O is performed at a poly(1-vinylimidazole-*co*-acrylamide)-[Os(dichloro-bpy)$_2$Cl]/bilirubin oxidase biocathode.[2] Redox polymers and enzymes were immobilized on the electrodes via a straightforward drop-cast process. The electrochemically deposited neutral PEDOT films reveal a blue color and turn transparent upon oxidation by the glucose-limited current of the connected biofuel cell (Figure 1b). Since the power output generated by the biofuel cell is used to oxidize the PEDOT film, this sensing device excludes any necessity for external powering devices, thus reducing the complexity of the system and showing potential for applications as point-of-care device.

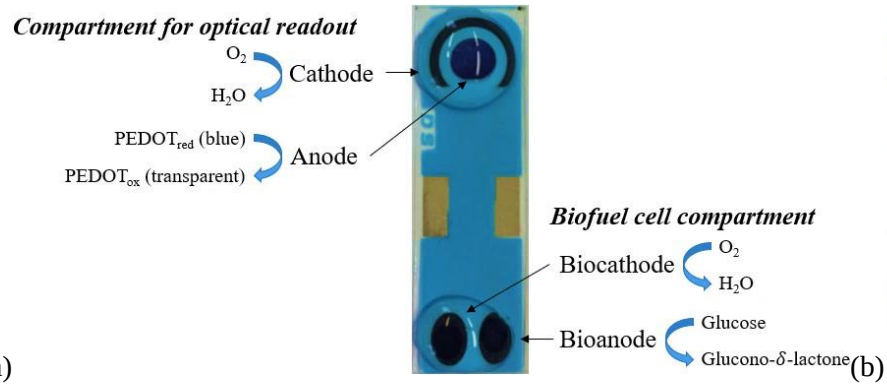

Figure 1. Screen-printed device for glucose detection with integrated biofuel cell coupled to an electrochromic reporter for optical readout. (a) Representation of the modified screen-printed device with indication of the electrodes assigned to the biofuel cell compartment and the compartment for optical readout, as well as to the involved key-reactions. (b) Decolorization of the electrochromic window upon addition of 50 mM glucose solution (C: Cathode, A: Anode, BC: Biocathode, BA: Bioanode)

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P03. **Characterizing *Escherichia Coli*-imprinted Polystyrene Thin Films with Confocal Raman Microscopy**

Birgit Bräuer, Felix Thier, Marius Bittermann, Dieter Baurecht, Peter Lieberzeit,

University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria
birgit.braeuer@univie.ac.at

The gram-negative bacterium *Escherichia coli* (*E.coli*) is considered an indicator of food and water safety.[1] Thus, various methods have been established to quantify and identify this microorganism, but they either lack sensitivity and selectivity, or require growth and enrichment of the bacteria. To address these issues, sensors suitable for direct detection of *E.coli* in water have been developed using molecularly imprinted polymers (MIPs) as an *E.coli*-sensitive layer on Quartz Crystal Microbalances (QCMs).[2] Surface characterization of MIPs is indispensable to ensure reproducibility of the polymer synthesis and assess the success of imprinting. Established techniques including Optical and Atomic Force Microscopy provide morphological characterization but no information about chemical composition of the surface.

We utilized Confocal Raman Microscopy to characterize *E.coli*-imprinted polystyrene synthesized using a covalent stamp imprinting approach. Performing Raman Image Scans on the polymer allowed us to obtain optical as well as spatially resolved chemical information about the sample surface. Overlaying Raman TV images (showing intensity distribution of the Raman signal at 2908 cm^{-1}) of *E.coli*-imprinted polystyrene before and after *E.coli* treatment and the corresponding white light images enabled straightforward differentiation between imprints, bacteria and polymer based on discrepancies in signal intensity at this wavenumber (Figure 1 A and B). Atomic Force Microscopy (AFM) was successfully used to assess accuracy of this distinction (Figure 1C) and to confirm success of the imprinting, which had been suggested by the Raman Image Scans.

Furthermore, we succeeded in successfully differentiating between two bacteria species, *E.coli* and *L.lactis*, on *E.coli*-imprinted polystyrene. For that purpose, we applied chemometric pattern recognition (Partial Least

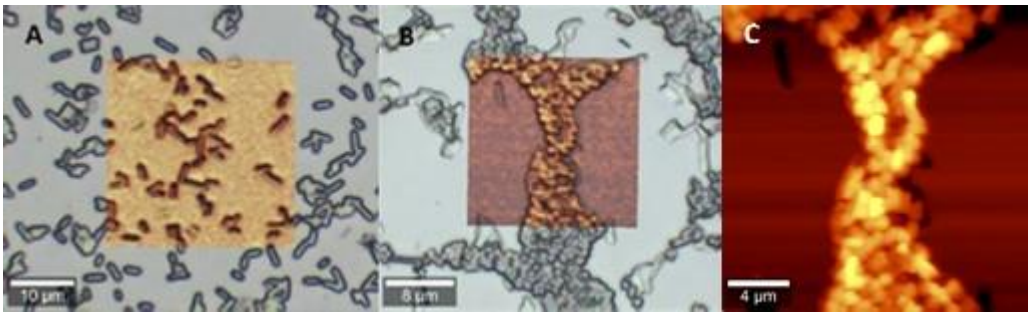

Figure 2. Overlays of Raman TV and white light images of A: E.coli-imprinted polystyrene and B: E.coli-imprinted polystyrene treated with E.coli; C: AFM image of E.coli-imprinted polystyrene treated with E.coli.

Squares Discriminant Analysis (PLS-DA) on Confocal Raman Images. This provides a basis for further selectivity studies of *E.coli*-imprinted polystyrene. The corresponding Raman spectra of the bacteria apparently exhibit spectral differences that, although they are not visible, can be extracted using PLS-DA and used to establish a model that can predict the affiliation of a bacterium to the *E.coli* or *L.lactis* class.

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P04. Reconstitution of Mitochondrial Membrane Protein in Liquid Crystal Phases

Aleksandra Buta,[a] Ewa Nazaruk,[a] Milena Krajewska,[b] Piotr Koprowski,[b] Adam Szewczyk,[b] Renata Bilewicz[a]

[a] University of Warsaw, Faculty of Chemistry, 1 Pasteur Street, 02-093 Warsaw, Poland
[b] Nencki Institute of Experimental Biology, Polish Academy of Sciences, 3 Pasteur Street, 02-093 Warsaw, Poland
abuta@chem.uw.edu.pl

The liquid crystal phases (mesophases) have specific properties and structure, e.g. the presence of a lipid bilayer surrounded by water channels, and a large internal surface ($400 m^2/g$). Such phases can be used to reconstitute amphiphilic membrane proteins. The immobilization of these molecules in phase provides them with a lipid environment similar to that of the biological membrane environment *in vivo*, thanks to which it is possible to study the structure and mechanism of protein activity.

We isolated a mitochondrial membrane protein - Renal Outer Medullary Potassium Channel 1 (ROMK1) from the bacterial culture (*Escherichia coli*). The quality of purification was checked by Western Blot and the protein concentration was determined by Bicinchoninic acid (BCA) method.

Protein immobilization was performed in mesophases containing monoolein (MO) or monopalmitolein (MP). These lipids differ from each other by the length of the lipid chain which affects the structure of the phase and the possibility of packing the protein inside it. The phase structure and the influence of protein incorporation were checked by Small-angle X-ray scattering (SAXS) method.

Studies of the activity of the ROMK1 protein inserted into the cubic phase include electrochemical methods. Chronoamperometry measurements will be done at different potentials applied to the electrode covered with the cubic phase membrane with and without ROMK1. The influence of potassium ion concentration and of the presence of thalium ion as the inhibitor will be presented.

P05. Wireless Biosensing of Analytes in Human Urine: Towards Smart Electronic Diapers

Stefan Cirovic, Magnus Falk, Sergey Shleev

Department of Biomedical Science, Faculty of Health and Society, Malmö University, Malmö, Sweden
stefan.cirovic@mau.se

Urinary incontinence is a common health problem among aged people, which require hospital staff to monitor patients. Leaving incontinence events unmanaged negatively impacts patient´s mental and physical health. To alleviate the problem, there is a need and a desire to have an incontinence detection system or device to alert a caregiver when it is time to change diapers. Automatic detection systems can significantly improve incontinence management, moving from a predominantly manual to an automatic process. A variety of different systems have already been developed that achieve wireless urinary incontinence monitoring, detecting the presence of moisture.[1,2] Instead of being used solely as wetness sensors, such systems could greatly benefit from also being able to detect different analytes of interest released in the urine.

By incorporating a biosensor in an electronic diaper, detection of different analytes can be achieved. The presence of glucose in urine results from the glomerular filtration of more glucose than the renal tubule can absorb, where abnormally increased amounts typically is associated with the disease diabetes.[3] Lactate is another very important prognostic marker, especially in critical patients, and urinary lactate have been shown to correlate with blood lactate.[4] A variety of other compounds with clinical relevance are also present in urine, such as urate, ascorbate, cholesterol and oxalate, all of which can be converted by different oxidoreductases.[3-5]

We design a wireless biosensing system for glucose and lactate in human urine, detected when present at elevated levels. To enable the wireless sensing, a previously developed wireless system for detecting moisture was modified with a conductometric biotransducer, giving a binary response that changes when the analyte is present at sufficiently high concentrations. The conductometric biotransducer is based on a Prussian blue – cellulose acetate layer, further modified with either glucose oxidase or lactate oxidase. In the presence of the substrates of the enzymes, hydrogen peroxide is produced which reacts with the layer, changing the conductivity of the Prussian blue – cellulose acetate layer from non-conducting to conducting state, which switches the response of the wireless sensing system. The system enables non-invasive analyte detection of urine samples, which could be used to design smart electronic diapers.

Acknowledgement:
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P06. Cubic Phase nanoparticles - Cubosomes as Carriers of Chemotherapeutics and Radionuclides

Adrianna Cytryniak,[a] Ewa Nazaruk,[a] Agnieszka Majkowska-Pilip,[b] Renata Bilewicz,[a] Aleksander Bilewicz [b]

[a] *University of Warsaw, Faculty of Chemistry, Warsaw, Poland*
[b] *Institute of Nuclear Chemistry and Technology, Warsaw, Poland*
acytryniak@chem.uw.edu.pl

Standard chemotherapy which acts on quickly dividing tumour cells can be ineffective due to the cancer drug resistance. It can also be the cause of healthy tissues damage and leads to dangerous side effects. To improve efficacy of the drug and minimize side effects the novel drug delivery systems are designed.

Lipidic liquid-crystalline phases (LCP), such as cubic phases, are promising as drug carriers since they have large interfacial area of 400 m^2/g and their structure consists of bicontinuous lipid bilayer surrounding two systems of non-contacting aqueous channels. A wide range of drugs can be encapsulated in this biocompatible amphiphilic environment resembling that of a biological membrane. The release rate of the drug from the mesophase can be modified by changing pH, temperature, pressure or phase composition.[1-3] Cubic phases are stable in the excess of water and can be dispersed in the presence of stabilizer into colloidal nanoparticles – cubosomes (Figure 1). Cubosomes are less viscous and exist as a suspension which makes them easier to handle and deliver to the appropriate site.[4]

We prepared cubic phases and cubosomes doped with doxorubicin (DOX) and characterised their structure by small-angle X-ray scattering (SAXS) and DLS (cubosomes). To investigate the behaviour of DOX incorporated into carrier and to determine drug release profile we used electrochemical methods. We considered Korsmeyer-Peppas and other mathematical models in the evaluation of the drug release kinetics. We also doped cubosomes with ^{177}Lu radionuclide and determined the labelling efficiency of the obtained system by means of instant thin layer chromatography (ITLC).

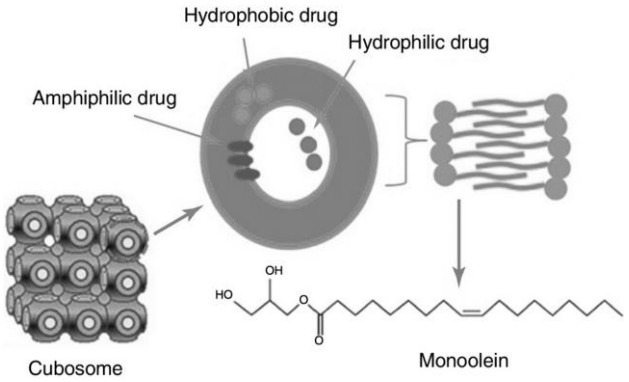

Figure 1. Structure of cubosome and possible location of drug depending on its propoerties.[5]

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P07. **Electrochemical Studies of DMPC-cholesterol Lipid Bilayer Supported on Au(111) Electrode Modified by 1-thio-β-D-glucose**

Damian Dziubak, Sławomir Sęk

Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw
Żwirki i Wigury 101, 02-089 Warsaw, Poland
ddziubak@chem.uw.edu.pl

Floating lipid bilayer membrane immobilized on the surface of a gold electrode is one of the models which can imitate the biological membranes. In this approach, the membrane is not directly contacted with the solid substrate but separated by a water-rich domain. This water reservoir is provided by the presence of the hydrophilic molecules which are used to pre-modify the electrode surface.

The gold surface modified by 1-thio-β-D-glucose[1] is able to mimic the quasi-natural environment of membranes and prevents transmembrane peptides and proteins from denaturation. It is possible due to hydrophilic properties of 1-thio-β-D-glucose (β-Tg) and presence of sulfur atoms in molecules, which enable to create stable and rich in water layer between the electrode and the lipid membrane. This approach has been used for example to investigate the pore-forming activity of alamethicin in DMPC bilayer,[2] or study properties of colicin E1, a channel-forming protein.[3]

In this work, we have monitored the process of vesicles spreading and formation of a bilayer consisting of DMPC and cholesterol (DMPC:Chol) on gold electrode modified with β-Tg by quartz crystal microbalance technic (QCM). We have also investigated capacitive behavior of Au(111)/β-Tg and Au(111) /β-Tg with DMPC cholesterol lipid bilayer by AC voltammetry and electrochemical impedance spectroscopy. Results show that the presence of lipid bilayer lowers the capacitance. However, its value is noticeably higher than for DMPC cholesterol directly deposited on Au(111) electrode. This is indicative of the presence of a thin water cushion between the electrode and the membrane. Using electrochemical QCM, we have investigated the mass changes vs. the applied potential for β-Tg, DMPC:chol lipid bilayer and for DMPC:Chol membrane on top of β-Tg. Our results confirm that upon desorption, the head groups of the inner layer detach from the metal and are separated by a thin cushion of water.[4] However, the same effect is also visible for Au(111)/β-Tg/DMPC:Chol.

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P08. Development of Whole Blood Vancomycin Sensor by Molecularly Imprinted Polymer-fixed Indium Tin Oxide Electrode

Haruto Eguchi,[a] Yasuo Yoshimi,[a] Akihiko Hatano[b]

[a] *Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan*
[b] *Shibaura Institute of Technology, 307 Fukasaku, Minuma-ku, Saitama 337-8570, Japan*
yosimi@sic.shibaura-it.ac.jp

Therapeutic drug monitoring (TDM) is strongly recommended for vancomycin (VCM), which is the first-line antibacterial agent against hospital-acquired infection. However, the conventional VCM analysis method is cumbersome in operation and forced to outsource inspection to external organizations, so the time lag of TDM is too long to for preventing resistant-bacteria creation. Therefore, we developed a VCM sensor for TDM which can measure rapidly and conveniently using molecularly imprinted polymer (MIP) which has a specific binding ability and can be produced easily and economically. We are developing a VCM sensor by fixing MIP on the indium tin oxide (ITO) electrode surface. In this study, we investigated the electron-mediation in a VCM sensor showing high sensitivity even in whole blood.

The VCM-MIP electrode was used to raise the VCM concentration while continuing the differential pulse voltammetry (DPV) measurement. The current value was plotted against the concentration of VCM in the measurement solution.We firstly examined the role of redox group (**Fig. 1**) included in the MIP. As shown in **Fig. 2**, the VCM-MIP electrode containing no redox monomer was insensitive to VCM, whereas VCM-MIP electrodes containing a ferroceneyl group were sensitive to VCM. The result indicates that the redox group as an electron transfer mediatorfrom VCM to ITO electrode. Therefore, it was found that redox monomer was necessary for VCM-MIP.

In order to confirm the response in whole blood, DPV measurement was performed using bovine whole blood as a measurement solution using an electrode containing ACPF. The results are shown in **Fig. 3**.

MIP electrode indicates same sensitivity in the whole blood and the buffer solution. However, a large background current was detected in the whole blood sample, which is probably due to coexisting redox species in blood. Thus, measurement was performed using washed blood cells suspension and plasma as measurement solutions. In plasma, the current intensity of the section was almost the same as in whole blood, whereas in the washed blood cells suspension, that was almost the same as in the buffer solution. The result indicates that a large background current is due to the plasma component. Thus, it is considered that the VCM concentration in the whole blood can be measured by subtracting the current intensity caused by the plasma component from the current intensity in the whole blood.

VCM sensing is possible by including ferrocene in the VCM-MIP electrode. Furthermore, by correcting the current value due to the plasma component, this electrode can perform VCM sensing in whole blood.

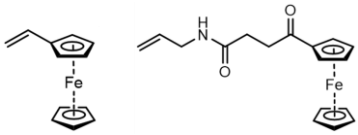

Fig. 1 Structural formula of redox group ; Vinyl ferrocene (left) and ACPF (right)

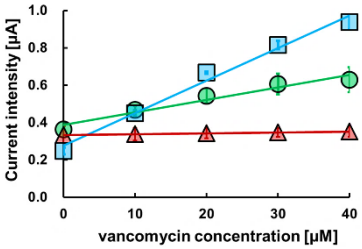

Fig. 2 Effect of VCM concentration on anodic current at the MIP electrode prepared with a redox monomer of Vinyl ferrocene(○), ACPF(□), or none(△).

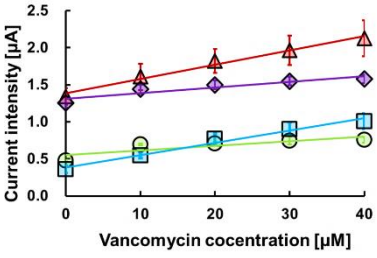

Fig. 3 Relationship between current intensity and VCM concentration in bovine whole blood (△), buffer saline (□), washed blood cells suspension (○) and plasma (◇).

P09.

The Regeneration of NAD(P)H Cofactor: Electrochemical Process for Biosynthetic Applications Loaded by a Functionalized Electrode

Wassim El Housseini,[a,b,c] Françcois Lapicque,[b] Elisabeth Lojou,[c] Neus Vilà,[a] Alain Walcarius,[a] Mathieu Etienne[a,*]

[a] *Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement (LCPME), Villers-lès-Nancy, France*
[b] *Laboratoire Réactions et Génie des Procédés (LRGP), Nancy, France*
[c] *Bioénergétique et Ingénierie des Protéines, Marseille, France*
**mathieu.etienne@univ-lorraine.fr*

There is a growing interest for the regeneration of the cofactor NAD(P)H due to its large-scale biosynthetic applications and its high price. Different methods including: chemical, electrochemical, photochemical, microbial, and enzymatic reactions have been developed for this aim. Among all the cited cofactor's regeneration methods, the electrochemical regeneration is a continuous electron-transfer process, where the regeneration of NAD(P)H is loaded only with an electrode. In our work, we have demonstrated an enzymatic bioreactor for simultaneous electrosynthesis and electricity production.[1] In order to perform the bioreactor, two electrodes are involved: a carbon felt bioanode modified by multi-walled carbon nanotubes (MWCNT) containing D-sorbitol dehydrogenase immobilized in a silica matrix offering high stability for a long time and an oxygen gas flow cathode. Two reactions were involved in the bioanodic compartment: the regeneration of NADH simultaneously followed by the bioconversion of D-sorbitol into D-fructose. In addition, the bioconversion of D-sorbitol proved that the regenerated NADH was active. The co-immobilization of the enzyme which helps in reducing waste production and the mediator used (poly (methylene green)) electrodeposited on the carbon felt/MWCNT electrode) allowed a regioselective conversion of D-sorbitol with high rates (1.65 $mg.day^{-1}.cm^{-3}$) and with a peak power of 14.6 $\mu W.cm^{-3}$ at 0.1 V without the need for the usage of a membrane.

Having achieved this first point of the study, actually, our work is now focusing on the reverse reaction. Here, we are studying the regeneration of NADH on the cathodic compartment. To begin our study, an electrode for this purpose was prepared using carbon bucky paper where a rhodium complex mediator was either immobilized on the carbon bucky paper surface or used in solution. The covalent immobilization of the rhodium complex ($[Cp^*Rh(bpy)Cl]^+$) on the surface of a bucky paper electrode was achieved by following a two steps protocol described by us recently.[2] A bipyridine ligand was first grafted on the electrode by electro-reduction of bipyridyl diazonium cations generated from 4-amino-2,2′-bipyridine, and the complex was then formed by reaction with $[RhCp^*Cl_2]^{2+}$. The work started with the study voltammetric responses obtained after the addition of a quantity of NAD^+ in order to prove the feasibility of the reaction. Then, the study was continued by measuring the obtained quantity of NADH through UV-visible technique at 340 nm and pH of 6.3.

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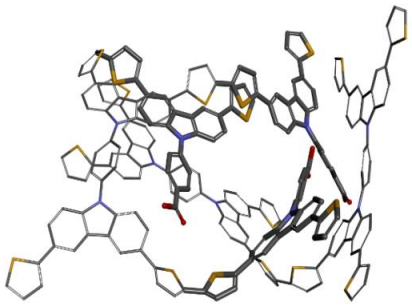
P10. Moleculary Imprinted Polymer as a Recognition Layer in Chemosensor Selective towards Aripiprazole

Marianna Gajda,[a] Maciej Cieplak,[a] Renata Rybakiewicz,[b] Teresa Żołek,[c] Dorota Maciejewska[c], Edyta Gilant,[d] Katarzyna Tyszko,[d] Piotr J. Rudzki[d], Andrzej Kutner,[d] Jyoti,[a,b] Paulina Wilczyńska-Materska,[a] Włodzimierz Kutner,[a,b] Krzysztof Noworyta[a]

[a] *Physical Chemistry Institute Polish Academy of Science, Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Department of Mathematics and Natural Science, School of Science, Kardynal Stefan Wyszyński University, Wóycickiego 1/3, 01-938 Warsaw, Poland*
[c] *Department of Organic Chemistry, Faculty of Pharmacy, Medical University of Warsaw, Banacha 1, 02-097 Warsaw, Poland*
[d] *Pharmacokinetics Department, Łukasiewicz Research Network - Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warsaw, Poland*

Aripiprazole is a partial agonist of dopaminergic receptor D2, serotoninergic receptor 5HT1 and antagonist of serotoninergic receptor 5HT2, used for treatment of schizophrenia and bipolar affective disorder.[1] Currently, to determine the active substance levels in plasma we use capillary electrophoresis and high performance liquid chromatography with spectroscopic or mass spectrometric detection.[2-5] Those methods are expensive and require special equipment, qualified personnel and high purity chemicals and reference standards.Thus, there is a need to develop new selective and reliable methods to determine medicines in biological matrices.



Scheme 1. Interaction of aripiprazole with functional monomers.

The aim of the study was to design easy to use selective chemosensor for aripiprazole using the Molecularly Imprinted Polymer (MIP) film as a recognizing element. The key task in the development of the MIP sensor is choosing correctly functional monomers.[6] We applied thiophene modified carbazole derivatives which electropolymerize in low potentials. Thus, we avoided the risk of simultaneous oxidation of aripiprazole during the preparation of the MIP. We have carried out DFT calculations, which allowed selecting the monomers that form the strongest complex with the analyte and to estimate the right composition of the polymerization mixture. This mixture was used to deposit the MIP film on the platinum electrode using electropolymerization. Subsequently, extraction of the template was established. Deposited films were characterized at each step of the synthesis. Electrodes covered with MIP film were used to determine aripiprazole using electrochemical signal transduction method.

To allow comparison with classic techniques we have developed novel bioanalytical method for determination of aripiprazole and its main metabolite dehydro-aripiprazole in human plasma. Analytical range of our liquid chromatography – mass spectrometric (LC-MS) method was selected to cover concentrations expected in human plasma of patients treated with standard oral doses of aripiprazole.

Acknowledgment:
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P11. **Preparation of Highly Organized Layers of ZnO Nanoparticles for Potential Application in Chemosensors**

Karolina Gołębiewska,[a] Edyta Pieńkowska,[b] Zbigniew Wróbel,[a] Dominik Kurzydłowski,[b] Paweł Borowicz,[a] Krzysztof Noworyta[a]

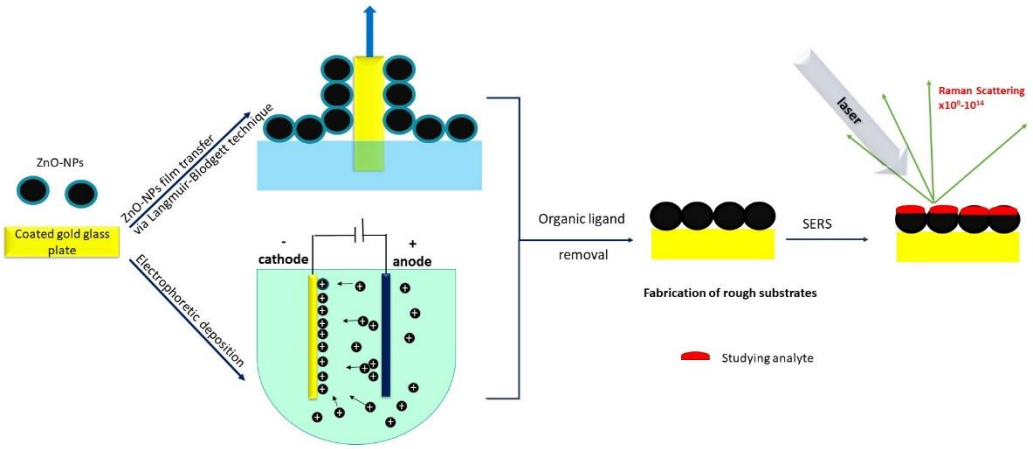
[a] *Institute of Physical Chemistry Polish Academy of Sciences, Kasprzaka 44/52 01-224 Warsaw, Poland*

[b] *Cardinal Stefan Wyszyński University in Warsaw , Wóycickiego 1/3 01-938 Warsaw, Poland*

kgawecka@ichf.edu.pl

The dynamic development of nanotechnology results in obtaining new materials and hybrid materials with new properties and a wide spectrum of application. Zinc oxide nanoparticles (ZnO-NPs) are a wide-bandgap semiconductor with a gap energy of 3.37 eV. ZnO NPs are phenomena in scientific and technological field of research due to their optical and electrical properties. Hence, nanomaterials based on ZnO-NPs are used in many different devices such as nanolasers, chemical sensors (including gas-sensor).[1] Biodegradability and low toxicity of ZnO NP-s increased attention toward their use in pharmacology and medicine, for example in vivo imaging with fluorescent probes based on quantum dots.[2]

The main goal of this work was deposition of thin films of ZnO-NPs stabilized with organic ligands on solid substrates. Two techniques were used for this purpose: Langmuir-Blodget technique and electrophoretic deposition. Both techniques allows for control of the layer thickness which leads to the formation of reproducible and homogeneous substrates without additional impurities. The ZnO-NPs stabilized with butylamine of 5 nm diameter were used in the current work. Fabricated substrates were tested for their potential application in Surface Enhanced Raman Spectroscopy (SERS). The SERS allows for detection of even single molecules deposited on highly rough substrate. Therefore, this technique is of great interest as transduction method in chemosensors.[3]



Scheme 1. Fabrication of the rough substrates for SERS.

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P12. Spin Filter Properties of Chiral Thin Film Highlighted by an External Magnetic Field

S. Grecchi,[a] S. Arnaboldi,[a] M. Magni,[a] T. Benincori,[b] C. Fontanesi,[c] R. Cirilli,[d] S. Cauteruccio,[a] E. Licandro,[a] P. R. Mussini[a]

[a] *Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19 20133, Milano, Italy.*
[b] *Università degli Studi dell'Insubria, Dipartimento di Scienza e Alta Tecnologia, Via Valleggio11, 22100, Como, Italy*
[c] *Università degli Studi di Modena, Dipartimento di Ingegneria "Enzo Ferrari", via Vivarelli 10, 41125, Modena, Italy*
[d] *Istituto Superiore di Sanità, Centro Nazionale per il Controllo e la Valutazione dei Farmaci, Viale Regina Elena 299, Roma, Italy*
sara.grecchi@unimi.it

The study of the mutual influence between chirality, electron spin and magnetism is a well-documented field of research, in fact implications span from pure fundamental research, to chemical applications of both analytical and synthetic character, to multidisciplinary purposes.[1,2] In this context the interrelated disciplines of magnetoelectrochemistry, spintronics and Spin Dependent Electrochemistry (SDE) play a crucial role. In particular, the combination of spintronics with magneto- electrochemistry, involving truly chiral molecular spin selectors, was promoted by the discovery of the Chiral Induced Spin Selectivity (CISS) effect by Ron Naaman and coworkers, observing spin polarization in photo-ejected electrons transmitted through a thin layer of enantiopure material adsorbed on gold, acting as an electron spin filter.[3]

Our proposed strategy is a variation of the SDE protocol, in fact the innovative set-up involves *i)* a non-ferromagnetic electrode (ITO as working electrode) covered by thin electroactive chiral films as electron source, *ii)* achiral redox couples dissolved in aqueous or organic solutions and *iii)* an external permanent magnet which was placed perpendicular to the electrode surface, considering as spin filters four different types of chiral selectors (with different stereogenic elements, *i.e.* helix, stereogenic axis and chiral pendant).[4-6]

A spectacular unforeseen effect was observed performing cyclic voltammetry (CV) experiments under applied magnetic field, in fact the CV peaks of achiral, chemically reversible redox couples undergo impressive potential shifts by flipping the magnet orientation (north *vs* south), with specular results changing the film configuration.

The importance of these studies includes possible applications in the field of spintronics, electronics, chemical sensoristic and so on and provides a striking evidence of the spin selectivity properties of chiral thin films.

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P13. A Novel Approach to Study Electrode Response in the Presence of Interfering Species – Towards Non-enzymatic Glucose Sensing

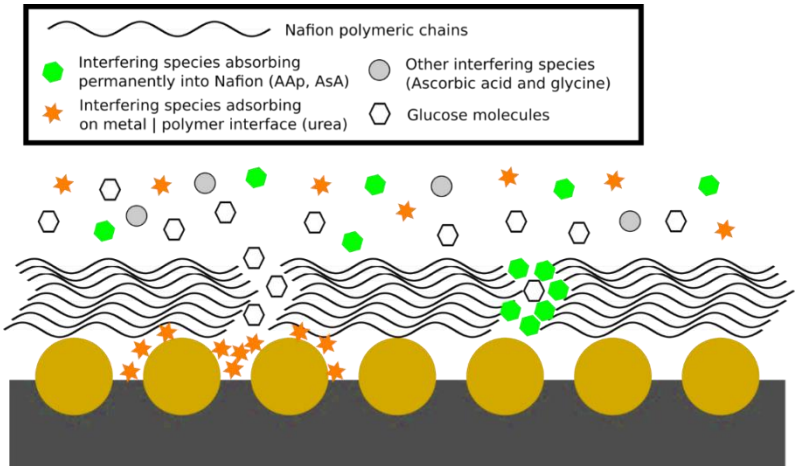
Adrian Olejnik,[a] Katarzyna Siuzdak,[a] Anna Dołęga,[b] Katarzyna Grochowska[a]

[a] *Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszera 14 st., 80-231 Gdańsk, Poland*

[b] *Department of Inorganic Chemistry, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12 st., 80-233 Gdańsk, Poland*

Currently, because of the rapid increase of people suffering from diabetes, one may observe many efforts put to elaborate highly sensitive materials towards glucose. However, preliminary verification of their activity is carried out in the pure glucose solution without any additives. Regarding glucose sensing in the real samples like blood, saliva or interstitial fluid, one should be aware of different interfering species that could significantly impact onto the electrode material, particularly its sensitivity and selectivity. To overcome this problem, typically, the electrode is coated with ion selective membrane. Among others, Nafion is commonly used due to its biocompatibility and excellent film forming ability.

In here, we present a novel approach to analyze the mechanisms of interference phenomena in glucose sensing taking into account the changes within Nafion layer deposited onto the active surface. Heterostructure composed of Au nanoparticles embedded in the cavities of textured titanium foil is used as a model sensing platform further coated with Nafion membrane. Electrochemical techniques, including electrochemical impedance spectroscopy and cyclic voltammetry were used to verify the sustainability of catalytic properties of the material after exposure to different compounds, i.e. ascorbic acid (AA), glycine, urea, acetylsalicylic acid (AsA) and acetaminophen (AAp). Through analysis of impedance data we concluded that AAp and AsA are trapped permanently into Nafion membrane, that significantly affects repeatability of the measurements. Those observations are also confirmed by FTIR investigations of the membrane after its exposure to solutions containing different interfering species. Moreover, after testing of the electrode in AsA containing solution and, unexpectedly, large concentrations of urea catalytic properties are completely lost. Mechanisms involving adsorption onto the interphase and absorption into the membrane pores were proposed as responsible factors for such behavior (see schematic representation below).



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P14. **Fluorescence Microscopy of mCherry Photoactive Protein**

Justyna Grzelak,[a] Martyna Domagalska,[a] Artur Ziółkowski,[a] Karolina Sulowska,[a]
Joanna Niedziółka-Jönsson,[b] Sebastian Maćkowski[a,c]

[a] *Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland*
[c] *Baltic Institute of Technology, Gdynia, Poland*
justynag@fizyka.umk.pl

Photoactive proteins, including photoconvertible and photoswitchable proteins, form a class of structures with unique and exciting properties.[1] Combining them with nanostructures, such as plasmonically active metallic nanoparticles,[2] offers a possibility to construct systems with new functionality.

In this work we study the photophysics of several photoactive proteins using fluorescence microscopy and spectroscopy. In addition to standard ensemble measurements, we have carried out also single-molecule studies in order to understand the influence of excitation wavelength on the photostability in various matrices. Also, we have fabricated a hybrid nanostructure with single proteins attached to silver nanowires. Fluorescence microscopy proves that the emission of these proteins is increased due to the plasmonic coupling with excitations in the nanowires. An important step towards controlled assembly of such systems has been developed by depositing microdroplets on silver nanowires. In this way the optical properties of the photoactive proteins can be remotely controlled with defined excitation wavelength. Consequently, the experiments show that it is possible to control the fluorescence of photoactive proteins both via plasmon resonance and remote excitation with precisely tuned excitation wavelength.

Acknowledgements:
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P15.

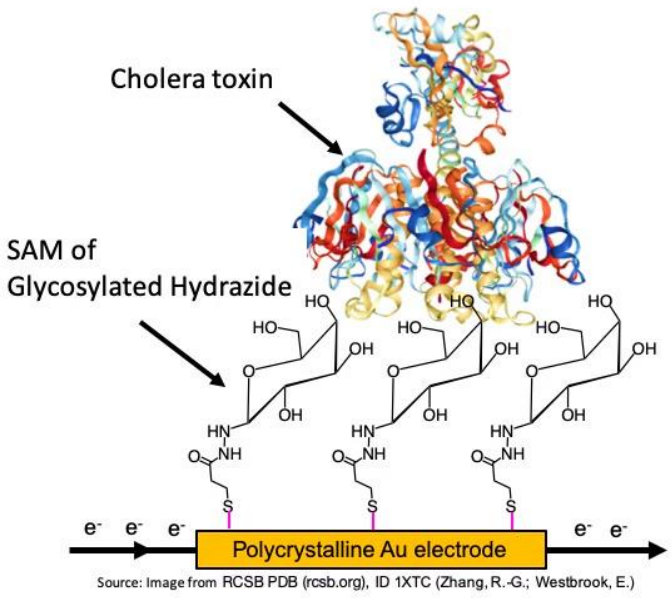
Functionalization of Au Electrodes with Glycosylated Hydrazides for the Electrochemical Detection of *Vibrio cholerae* Toxin

C. Guillén Posteguillo, A. Kołodziej, F. Fernández-Trillo, P. Rodríguez

University of Birmingham, Birmingham, United Kingdom
cxg623@student.bham.ac.uk

The World Health Organization (WHO) estimates that millions of people fall ill and thousands die every year after ingesting contaminated food or water;[1] most cases of food poisoning are caused by bacteria.

Current standard methods of detection of bacteria, although reliable, present features that make their use difficult or impossible in rural areas, regions with poor health infrastructure or conflict zones. Furthermore, phenomena like climate change, globalization or the aging of the world population have increased the risk of food poisoning, for *e.g.* in the aftermath of increasingly frequent natural disasters.[2] Electrochemical biosensors represent an alternative thanks to their sensitivity but also simplicity, low-cost and portability.[3]



In this work the first steps of development of an electrochemical biosensor for the detection of the toxin of *Vibrio cholerae* in aqueous media are presented. The design of the device aims at mimicking the recognition mechanism of the toxin in the human intestinal cells.[4] Polycrystalline electrodes have been functionalized with self-assembled monolayers (SAMs) of organic molecules (hydrazides) that will be chemically linked to galactose. The interaction of the toxin with the saccharide will induce changes in the electrodic process on the electrode surface generating an analytical signal for the detection of cholera. This biosensor will serve as a proof-of-concept for the construction of analogues for other pathogens.

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P16.

Molecularly Imprinted Polymer Thin Film for Selective Detection of Penicillin G in Aqueous Samples

Shahin Haghdoust, Peter Lieberzeit

University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria
Shahin.haghdoust@univie.ac.at

Penicillin G is a widely used antibiotic to treat and prevent bacterial infection effectively. However, release of antibiotics into aquatic environments among others is associated with the risk of increased antibiotic resistance.[1] In order to protect public health, rapid, accurate and specific sensing is strongly desired. To achieve this purpose, molecular imprinting is a technique to design robust receptor materials that are able to mimic natural recognition species.[2] Herein we report a molecularly imprinted polymer (MIP) to detect penicillin G (PenG) by quartz crystal microbalance (QCM).

The necessary MIP thin films were synthesized by radical polymerization of methacrylic acid (MAA) as the functional monomer, and ethylene glycol dimethacrylate (EGDMA) as the cross-linker; after thermal polymerization at 60°C, the polymer was spin-coated onto QCM electrodes. The non-imprinted (NIP) sample was prepared in the same manner without template. Figure 1a shows the resulting QCM sensor characteristics: It clearly reveals concentration-dependent sensor signals of the system. Moverover , responses are fully reversible. MIP-coated electrodes reach about five times the frequency shifts of NIP-coated ones. Furthermore, the MIP are selective: Figure 1b shows the outcome of selectivity studies toward Penicillin V and Amoxicillin, which demonstrate selectivity factors of around 1.5 each. This is even more remarkable given how similar the molecular structures of those three compounds are. Finally, sensor characteristics reveal limit of detection at 0.015 mg/ml. The sensors hence lead to appreciable results illustrating the potential of the approach for further work.

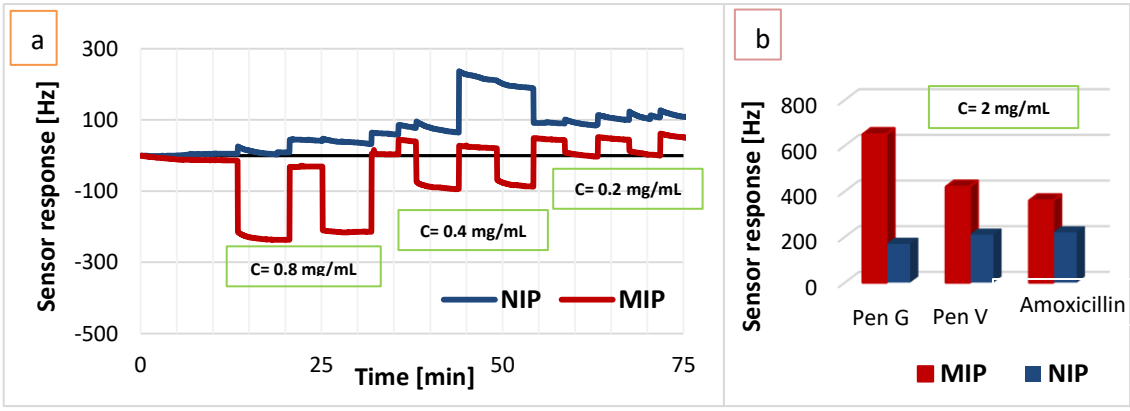

Figure 3. a) QCM sensor responses of MIP and NIP, respectively, toward PenG; b) Selectivity pattern of sensors at c=2 mg/ml.

Acknowledgement:
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P17. Biofunctionalization of a Microring Resonator via Hydrosilylation Followed by Copper Free Click Chemistry

Anders Henriksson,[a] Peter Neubauer,[a] Mario Birkholz[b]

[a] *Technische Universität Berlin, Institute of Biotechnology, Chair of Bioprocess Engineering, Ackerstrasse 76, 13355 Berlin, Germany*
[b] *IHP - Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, D - 15236 Frankfurt (Oder), Germany*
henrikson@tu-berlin.de

Silicon on insulator (SOI) micro-ring resonators are one of the more interesting techniques developed for label free sensing during the last decade. It benefits from well-known standardized and scalable semiconductor fabrication processes, and enables real time responses, minimal footprints and extraordinary sensitivity. Essential for the development of high-performance sensors is a surface modification strategy that generates a sensor surface that facilitate both molecular interaction as well as the generation of a large optical resonance shift. The general surface chemistry approaches are based on ω-functional silanes that binds to the native oxide of the silicon surface followed by biomolecule immobilization via standard coupling reactions. While the approach is reliable and simple, this strategy functionalizes not only the active sensor surface but also the enclosed buried oxide layer (BOX), thus wasting receptor molecules and potentially decreasing the sensitivity of the device. In this study we have explored a copper free click chemistry approach[1] as a bioconjugation method and the hydrosilylation reaction as an alternative to silane-based surface functionalization strategies that is selective for the silicon surface.

An electron deficient dialkyne was grafted to the ring resonator via thermal induced hydrosilyation to form an alkyne terminated surfaces. Green fluorescent protein labeled with azido functionalities was subsequently coupled to the sensor surface via copper free click chemistry at 40 °C. The functionalization was followed optically via a resonance shift of the ring resonators and by ellipsometry. The copper free click chemistry approach was preferred over the state-of-the-art copper catalyzed reaction, as the later resulted in substantial copper deposition onto the sensor chip.

The presented protocol may be useful for the biofunctionalization of a large variety of SOI microchips, were functionalization of the silicon oxide are to be avoided.

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P18. On the Role of Cholesterol in Perifosine Action on Model Lipid Rafts

Joanna Juhaniewicz-Debinska, Kinga Burdach

Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw
Zwirki I Wigury 101, 02-089, Warsaw, Poland
jjuhaniewicz@chem.uw.edu.pl

Cancer diseases are one of the main causes of death, right after cardiovascular diseases. Their number is steadily growing despite extensive development of new drugs and therapies. Synthetic antitumor lipids (ATLs) are a promising group of compounds in cancer chemotherapy.[1] They can be divided into two main classes: alkylphospholipids (APLs) and alkylphosphocholines (APCs). They are structurally similar to a naturally occurring lysophosphatidylcholine and possess distinct antiproliferative properties in tumor cells.[2] APLs and APCs do not interfere with the DNA but incorporate directly into cell membranes, where they accumulate and disturb lipid metabolism and lipid-dependent signalling pathways.

Perifosine (octadecyl-(1,1-dimethylpiperidinio-4-yl)-phosphate) is one of alkylphospholipids analog with promising results against a variety of cancers. The studies showed that perifosine accumulates in specific domains in cell membranes called lipid rafts.[3] These membrane microdomains enriched in cholesterol and sphingolipids are the platform of several signalling pathways, including the Akt pathway, one of the most frequently hyperactivated signaling pathways in human cancers and, therefore, a very important target in a global fight against this disease.

The aim of the present study was to assess the effects of perifosine on model lipid membranes reflecting the lipid composition of natural lipid rafts. Model lipid rafts were composed of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), sphingomyelin (SM) and cholesterol (Chol). Firstly, the effect of cholesterol on perifosine action on model lipid raft was studied. For this purpose, we prepared model lipid rafts with 0 – 50 % cholesterol content. We have also verified the effect of gangliosides on the perifosine – lipid membrane interactions. Results of Langmuir studies show that perifosine incorporate in model lipid membranes at the air-water interface and the effect of perifosine increases with increasing cholesterol content. The changes in the morphology of the lipid layer in the presence of perifosine were also monitored by Brewster Angle Microscopy. In the next step, solid-supported lipid bilayers were used to obtained more detailed information on perifosine-lipid interactions. We employed the combination of Langmuir-Blodgett and Langmuir-Schaefer techniques to immobilized model lipid membranes on the solid support. Quartz crystal microbalance with dissipation monitoring allowed us to observe the kinetics of the perifosine-membrane interactions and to verify the mechanism of perifosine-induced perturbations within the lipid membrane.

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P19. Synergy of Surface and Semi-covalent Imprinting for Chemosensing of Gonadotropin Protein Hormone

Jakub Kałęcki, Marcin Dąbrowski, Maciej Cieplak, Piyush Sindhu Sharma

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
jkalecki@ichf.edu.pl

Family of gonadotropin hormone includes human chorionic gonadotropin (hCG), luteinizing hormone (LH) and follicle-stimulating hormone (FSH). The latter hormone stimulates the maturation of the primordial germ cells in women and men. Both lowered and elevated levels of FSH in the blood are associated with disease states. Therefore, interest in the determination of fertility hormones has steadily increased.

Molecular imprinted polymers (MIPs) are synthetic biomimetic receptors which are capable of binding target molecules with an affinity and specificity similar to natural receptors. These materials integrated successfully to transducer surface for fabrication of chemosensors. However, conditions normally used for imprinting of small molecule can bring conformational change in proteins. Additionally, bulky proteins are difficult to remove from cross-linked polymer.

Therefore, to enhance the number of binding sites and for easy removal of proteins from imprinted cavities we adopt combination of surface and semi-covalent imprinting. Towards that, we first immobilize the protein on silica substrate through an anchor layer. Later, we labelled the immobilized protein with functional monomer. This labelling was possible through amide chemistry. In final step, we electrochemically cross-linked functional monomers with excess of cross-linking monomer.

One step further, in current work, we have optimized conditions for preparation of a stable homogeneous colloidal crystal structure with surface modified silica beads of 500 nm diameter.[1] We confirmed regular and hexagonal packing of silica beads and resulted inverse opal surface imprinted molecular imprinted film by scanning electron microscope (SEM). Successful modification of silica with protein through imine bonds, as well as protein derivatizing with functional monomers through amide bonds, were confirmed by X-ray photoelectron spectroscopy (XPS). The recognition of FSH by the macroporous molecularly imprinted polymer film was transduced with the help of capacitive impedimetry. Ultra level sensitivity was achieved by synergetic combination of silica molding, surface and semi-covalent imprinting. This synthetic receptor, was further used for selective determination of FSH in artificial blood serum samples.

Acknowledgments:
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P20. **Study of Human Growth Hormone Antibody Layered Structures with Scanning Electrochemical Microscopy**

A. Kisieliute,[a] J. Petroniene,[a] I. Morkvenaite Vilkonciene,[ab] W. Nogala,[c] A. Popov,[a] B. Brasiunas,[a] A. Ramanaviciene,[a] A. Ramanavicius

[a] *Faculty of Chemistry and Geosciences, Vilnius University, Vilnius, Lithuania*
[b] *Faculty of Mechanics, Vilnius Gediminas Technical University, Vilnius, Lithuania*
[c] *Institute of Physical chemistry, Polish Academy of Sciences, Warsaw, Poland*
aura.kisieliute@gmail.com

Constant advancement towards biochemical sensing improves the quality of medical devices used for evaluating diseases, pharmaceutical components and thus helping patients in need[1]. Researches are interested in improving bioanalytical systems for better detection of targeted molecules, lowering their detection limit, making the devices cheaper or re-usable and eco-friendly[2]. One of such devices are immunosensors or immunoassays which detect molecules through the use of antibodies or antigens[3].

In our study we were investigating layered structures of human growth hormone antibodies with scanning electrochemical microscopy (SECM)[4]. The antibodies were labelled with an active enzyme- glucose oxidase for recognizing the areas where they were immobilized. By scanning the layered structures with the SECM and with the redox mediator, glucose present in the solution we could detect the electrochemically active areas. This method could help study the antibody-antigen interactions.

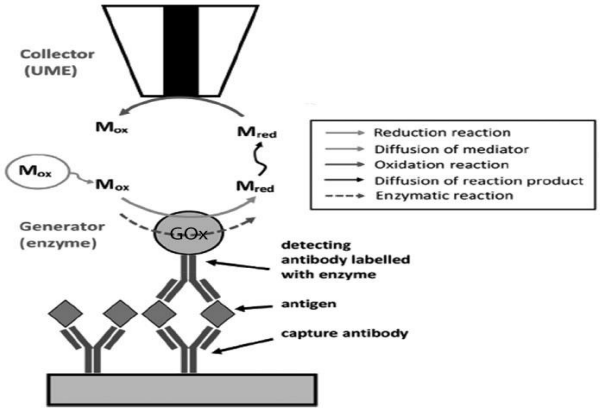

Fig. 1. A schematic representation of enzyme labelled antibody detection with SECM

This technique with further future development could help detect and evaluate the concentration of human growth hormone present in human biological fluids. It could be useful for dopamine testing in athletes or as a medical assay for growth disorders.

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P21. The Influence of Modified Cyclodextrin on the Anthracycline Binding to DNA

A. Krzak,[a] M. Majdecki,[b] O. Święch,[a] R. Bilewicz[a]

[a] *University of Warsaw, Faculty of Chemistry, Warsaw, Poland*
[b] *Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland*
agata.krzak@chem.uw.edu.pl

Anthracycline antibiotics (ANT), are most commonly used anticancer agents for the treatment of several types of cancers. Clinical effects of the drugs are connected with modification of the DNA structure primarily through intercalating complexes and covalent bonding.[1,2] However, the clinical application of doxorubicin has been limited by serious adverse effects.[3,4] The specific toxicity of the drug is due to reactive oxygen species (ROS) produced in redox reactions of anthracycline. The radical oxygen species can interact with cellular components such as proteins, lipids, carbohydrates or nucleic acids. All of the modifications can cause mutation of the healthy cells. The toxicity can be reduced e.g. by creating an inclusion complex holding the anthracycline molecule inside a cyclodextrin (CD) cavity.

The limitation in the use of CD as a carrier of anthracycline drugs is the low stability of the complex. We showed earlier that appropriate modification of the cyclodextrin can increase the stability of the drug-CD inclusion complex. The derivatives of β-cyclodextrin with a triazole moiety formed strong inclusion complexes with ANT with 1:1 stoichiometry. Using voltammetry data we determined the stability constants of the complexes and we found their dependence on the pH: at pH 7.4, corresponding to the pH of body fluids, the stability constants were much larger than at pH 5.5, which is characteristic for cancer cells.[5-7] The question was how the modified CD affects the interactions of the drug with DNA – which are crucial for the therapy.

We present here newly designed nontoxic derivatives of β-cyclodextrin containing both antioxidant and targeting units in the molecule (lipoic acid, folic acid and galactosamine). We determined first the stabilities of the complexes of this new group of modified CDs with daunorubicin and doxorubicin, and next we evaluated the effect of these modified βCDs on the anthracycline interactions with DNA. Interestingly, the CD ligands were found to strengthen the drug–DNA intercalation both at pH 7.4 and 5.5. In the absence of cyclodextrins, binding of the anthracyclines to DNA is known to be much weaker at lower pH, which is a difficulty encountered in the therapies. We demonstrate that when the drug is complexed by appropriately modified cyclodextrins this effect is eliminated: the values of the stability constants of ANT-DNA are strong and similar at both pHs, The reasons of this phenomenon, important for potential therapeutic applications of the CD - based drug delivery, will be discussed.

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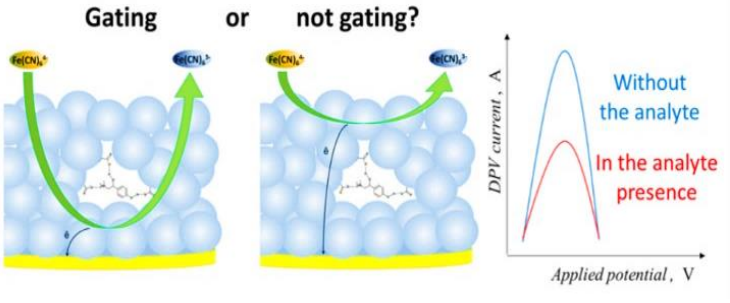
P22. **"Gate Effect" in Electrochemical Chemosensor Based on Conductive Molecularly Imprinted Polymer Using External or Internal Redox Probe**

Patrycja Lach,[a] Maciej Cieplak,[a] Marta Majewska,[a] Krzysztof Noworyta,[a] Piyush S. Sharma,[a] Francis D'Souza,[b] Wlodzimierz Kutner[a,b]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS), Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Department of Chemistry, University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, USA*
[c] *Faculty of Mathematics and Natural Sciences, School of Sciences, Cardinal Stefan Wyszynski University in Warsaw, Wóycickiego 1/3, 01-815 Warsaw, Poland*
plach@ichf.edu.pl

Molecularly imprinted polymers (MIPs) are excellent examples of bio-mimicking recognition materials.[1] They are widely applied for selective chemosensing. For electrochemical determination of electroinactive analytes, usually some external redox probe is added to the analyte solution. It is assumed that binding of target analyte molecules by MIP molecular cavities causes MIP film swelling or shrinking. This behavior leads to the so called "gate effect" which consists in changing of redox probe permittivity through the MIP film, thus changing faradaic currents in cyclic voltammetry (CV) and differential pulse voltammetry (DPV) determinations.[2]

Herein, we investigated the "gate effect" mechanism for conductive MIP film coated electrodes in detail. For that purpose, the polythiophene-based film imprinted with *p*-synephrine – a diet supplement that is suspected of causing serious cardiovascular diseases - was deposited on an electrode surface via electropolymerization under potentiodynamic conditions. It was demonstrated that the decrease of the DPV peak current for the $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and $Ru(NH_3)_6Cl_3$ redox probes with the increase of the *p*-synephrine target analyte concentration in the test solution did not originate from swelling or shrinking of the MIP film but from changes in the electrochemical process kinetics. The MIP-film coated electrode was examined by CV, DPV, electrochemical impedance spectroscopy (EIS), and surface plasmon resonance (SPR) spectroscopy. The MIP film thickness in both the absence and presence of the target analyte was examined with in situ atomic force microscopy (AFM). Moreover, it was demonstrated that doping of the MIP film is not affected by *p*-synephrine binding by MIP molecular cavities. The decrease of the DPV peak current was caused by the decrease of the electrochemical reversibility of the redox probe electro-oxidation. Therefore, the "gate effect" was most likely caused by changes in cation radical (polaron) mobility in the polythiophene MIP film.



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P23.

Targeted Nanoparticles for Diagnostic and Theranostic Applications.

Juan Leva-Bueno,[a] Ina Meuskens,[b] , Dirk Linke,[b] Sally Peyman,[b] Paul A Millner[a]

[a] *University of Leeds, UK*
[b] *University of Oslo, Norway*
bsjlev@leeds.ac.uk

Antimicrobial resistance (AMR) is a serious threat due to the rise of multidrug-resistant (MDR) bacteria.[1] Therefore, new technologies such as biosensing and lab-on-a-chip (LOC) devices have emerged in the last decades. Biosensing can detect and quantify biological analytes and combine high sensitivity and specificity with fast response times, portability, low-cost and ease-of-use.[2]

Two systems were studied through electrochemical impedance spectroscopy (EIS): on the one hand, a classic immunosensor[3] for *E. coli* was able to detect from 10^3 cfu/ml to 10^8 cfu/ml. On the other hand, a novel extracellular matrix (ECM)-based bioreceptor was investigated using YadA-expressing *E. coli* (O:8) as specific analyte.[4] ECM proteins are involved in the first-step of infection and it is thought that they can improve the homogeneity and reproducibility of antibodies as well as minimizing costs.

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P24. Studies of the Charge Transfer Kinetics and Surface Inhomogeneities of Enzyme-functionalized Au-Ti Electrode

Wiktoria Lipińska,[a] Katarzyna Siuzdak,[a] Jacek Ryl,[b] Paweł Ślepski,[b] Katarzyna Grochowska[a]

[a] *Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences, Fiszera 14 st., 80-231 Gdańsk, Poland*
[b] *Department of Electrochemistry, Corrosion and Material Engineering, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12 st., 80-233 Gdańsk, Poland*

Due to the fact that nowadays about 400 million people are diabetics and 1.5 million of them die each year, glucose detection in human body fluids contributes to many clinical tests and development of variety of biosensors.[1,2] Enzymatic electrochemical sensors represent the majority of such devices as they are considered as reliable. Typically their operating principle is based on potentiometric, amperometric or impedimetric measurements while the impedimetric approach is thought to be the most sensitive. Nevertheless, it should be considered that the errors associated with chosen technique affects its performance, while impedance measurement accuracy highly depends on selection of suitable electric equivalent circuit (EEC). It should be also noted that surface morphology affects the heterogeneity of distribution of electrochemical properties and hence the selection of appropriate EEC elements.

Therefore, we propose a novel approach for impedimetric measurements by applying dynamic electrochemical impedance spectroscopy in galvanostatic mode (g-DEIS), which allows to obtain key information regarding kinetic changes at the electrode/electrolyte interface during non-stationary processes.[3] The investigated material is composed of dimpled Ti plate where each cavity is filled with a single gold nanoparticle with anchored enzyme: glucose oxidase.[4,5] All electrochemical tests are performed in air-saturated 0.1 M PBS with the addition of different amounts of glucose within the concentration range of: 0-10 mM. It was shown that the increase of glucose content leads to slow decrease of functionalized layer capacitance. Additionally, charge transfer resistance changes are more dynamic for glucose concentrations below 3.9 mM as with the increase of sugar level in electrolyte the enzyme active centers become more occupied with glucose molecules. Moreover, the disturbance in the kinetics of the charge transfer versus glucose concentration function was confirmed through direct observation of constant phase element parameters, especially its exponent α reflecting surface homogeneity. It has been observed that below concentration of 1.9 mM glucose interaction with enzyme-functionalized electrode negligibly affects the charge transfer homogeneity, while at higher concentrations the electrode becomes more heterogeneous.

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P25. **Functional Plasma Polymerized Surfaces for Biosensing**

E. Makhneva,[a] L. Barillas,[a] Z. Farka,[b] M. Pastucha,[b] P. Skladal,[b] K. Fricke[a]

[a] *Leibniz Institute for Plasma science and Technology (INP), Greifswald, Germany*
[b] *Central European Institute of Technology (CEITEC), Brno, Czech Republic*
ekaterina.makhneva@inp-greifswald.de

Various types of biosensors are convenient tools for fast, economic and user friendly analysis of complex biological samples. For stable biomodification of the sensing surfaces, a thin functional layer is required to provide a sufficiently high surface reactivity towards the adopted bioreceptor, as well as good stability in the presence of sample matrix.

We report on the novel method of preparation of thin reactive plasma polymerized (pp) films for biosensing applications, using atmospheric pressure plasma jet (APPJ). Our original method for creation of pp films offers the advantages of a versatile, fast and eco-friendly procedure. The whole procedure takes just 1 min in total and does not require usage of any aggressive chemicals.

Three different types of pp films were developed and characterized. Chemical composition, morphology and stability in water of the obtained plasma polymerized films were carefully scrutinized. The obtained pp films provided unique functionality and excellent level of adhesion to the substrates. The tested pp films exhibited initial thickness losses during the first 24 hours of storage in water. Further prolonged immersion in water (up to 120 h) did not indicate any significant thickness losses or deterioration of the sensing properties.

SPR immunosensors were successfully developed, using cost-efficient model pair of AL01 antibody and HSA antigen. The pp films provided an excellent platform for the efficient immobilization of antibody molecules and the obtained immunosensors showed selective and high response towards analyte, excellent regenerability and level of stability. A limit of detection of 50 ng/mL of HSA was achieved for all of the developed immunosensors. The developed immunosensors provided a linear response in the range of 50 ng/mL to 20 µg/mL concentrations of HSA. The obtained results showed that the plasma polymerized film–based immunosensors have performance similar to widely used SAM– or CMD–based immunosensors. Plasma polymerized films though offer a better level of stability and regenerability.

P26. Chemosensor with Molecularly Imprinted Polymer Film as the Recognition Unit for Determination of Anticancer Drug Imatinib

Paulina Materska-Wilczynska,[a] Jyoti,[a,b] Renata Rybakiewicz,[b] Teresa Zolek,[c] Dorota Maciejewska,[c] Wlodzimierz Kutner,[a,b] Krzysztof Noworyta[a]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS), Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Faculty of Mathematics and Natural Sciences, School of Sciences, Cardinal Stefan Wyszynski University, Woycickiego 1/3, 01-815 Warsaw, Poland*
[c] *Department of Organic Chemistry, Faculty of Pharmacy, Warsaw Medical University, Banacha 1, 02-097 Warsaw, Poland*
pmaterska@ichf.edu.pl

Electrochemical chemosensor for selective imatinib determination with molecularly imprinted film as recognition layer was devised, fabricated and tested. For that purpose, we prepared by electropolymerization a molecularly imprinted polymer (MIP) film serving as the recognition unit of the chemosensor. The MIP film was based on polycarbazole derivatives.

Imatinib is a 2-phenylaminopyrimidine derivative acting as a specific tyrosine kinase inhibitor. It is widely used for treatment of chronic myelogenous leukemia, gastrointestinal stromal tumors and many other. Fast, simple and reliable method of this drug determination along with its principal active metabolites is important from the point of view of personalized drug dosage as well as pharmacokinetic studies of its transformations in the patient's body.

Molecular imprinting involves polymerization of a functional monomer and cross-linking monomer around a molecular template. Then, after template removal, we obtain molecular cavity which is able to bind the target molecule. Molecularly imprinted polymers (MIPs)-based chemosensors have numerous advantages, including high selectivity, stability, low limit of detection, robustness, and low cost.

In order to devise a selective MIP film, we have synthesized a series of electrochemically active carbazole derivatives which were then used as functional and cross-linking monomers. Interactions of selected carbazole monomers with the target analyte have been studied by Molecular Mechanics and DFT calculations. The calculation results allowed for better understanding of the molecular cavity formation process. Subsequently, the pre-polymerization complex was potentiodynamically electropolymerized resulting in formation of an electrochemically conductive polymer film. The deposited polymer film was characterized by spectroscopic, microsopic and electrochemical techniques showing differences between molecularly imprinted (MIP) and non-imprinted (NIP) polymer films. Extraction of a template was proven by using differential pulse voltammetry (DPV) and Fourier-transform infrared spectroscopy (FTIR).

The fabricated chemosensor response to imatinib was tested by using voltammetric techniques as well as electrochemical impedance spectroscopy. The chemosensor responded to changes in imatinib concentration from 10 to 300 μM. Tests were provided in both organic and aqueous solutions.

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P27.

Sensing of Nonconjugated Proteins at Charged Electrode Surfaces

Eva Melníková,[a] Nasim Izadi,[b,c] Miroslav Gál,[a] Veronika Ostatná[b]

[a] *Slovak University of Technology, Faculty of Chemical and Food Technology, Department of Inorganic Technology, Radlinského 9, 812 37 Bratislava, Slovakia*
[b] *Institute of Biophysics of the Czech Academy of Sciences, Královopolská 135, 61265 Brno, Czech Republic*
[c] *Department of Experimental Biology, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno Czech Republic*
eva.melnikova@stuba.sk

Different amino acid content and structure strongly affect proteins electrochemical behavior at charged surface. Ability to catalyze hydrogen evolution (CHER)[1] of five selected proteins (namely: human serum albumin, lysozyme, β-synuclein, histones H2A, and H3) was studied using electrochemical methods such as cyclic voltammetry (CV), chronopotentiometric stripping analysis (CPS) and phase sensitive alternating current (AC) voltammetry. Differences in proteins response at charged surface were due to its amino acid content, mainly cysteine[2] (Cys). We found out that appearance of peak H of Cys-containing proteins was at less negative potential in contrast to proteins not containing Cys residues suggesting easier CHER. Acidic and basic proteins without Cys after their adsorption at charged interface can be also recognized due to different CPS response. We also showed that CPS dependences of peak H height and potential of proteins on accumulation potential differed in comparison to almost equal peak H area.[3]

Acknowledgements:
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P28. **Conducting Metal-Polymers Based on Ru(II) Complexes as Modifying Agents for Electrode Surfaces**

F. Meloni, M. I. Pilo, G. Sanna, N. Spano, A. Zucca

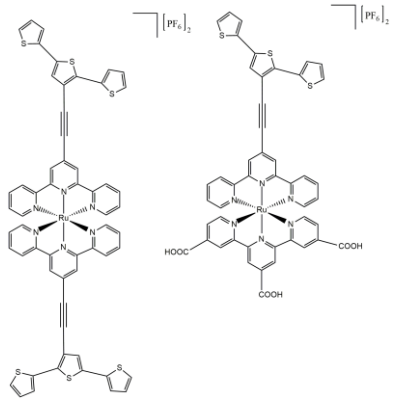
Department of Chemistry and Pharmacy, University of Sassari, Sassari, Italy
fmeloni1@uniss.it

Conducting metal-polymers can be considered hybrids between organic conjugated polymers and saturated polymers with transition metal complexes as pendants.[1]

Thus, this type of materials has also hybrid properties: the conjugated polymers conductivity is combined with the redox, optical and catalytic properties of the metal complexes in order to obtain synergic electronic interactions.

Thanks to these particular properties, the interest for these materials is increasing especially in the sensing and biosensing field.

Here, we report the use of two conducting metal-polymers based on Ru(II) complexes: poly[$Ru(TAT)_2$][2] and poly[(TAT)Ru(TpyCOOH)][3] (TAT = 4'-[(2,2':5,2''-terthien-3'-ethynyl]-2,2':6,2''-terpyridine; TpyCOOH = 4,4',4''-tricarboxylate-2,2':6,2'' – terpyridine) as modifying agents for electrode surfaces to assemble sensors and biosensors for histamine detection.



The idea of using poly[$Ru(TAT)_2$] is due to the peculiar characteristic of its monomer $[Ru(TAT)_2]^{2+}$: it can polymerize by anodic oxidation, as well as by cathodic reduction of terpyridine moiety generating a negatively charged film[2] which allows to exploit an attractive electrostatic interaction with protonated histamine (working in phosphate buffer solution pH 7,0) in order to gain an electrocatalytic effect.

The poly[(TAT)Ru(TpyCOOH)] was used because of its carboxylic groups in order to exploit an electrostatic interaction as the one just mentioned, working in the same conditions, but also to realize an enzymatic biosensor in which the enzyme can be linked to the polymer matrix through the formation of covalent bonds.

In particular, a platinum disk electrode covered with poly[(TAT)Ru(TpyCOOH)] on which diamine oxidase from *porcine kidney* has been immobilized, has proved to be an analytical tool with good linearity and sensibility and, to the best of our knowledge, it is one of the first second-generation biosensor based on diamine oxidase.

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P29.

Do Fats Matter?
Design of Serum Albumin Bioreceptor for PFOA, from Toxicological Studies to Biosensor Applications

Giulia Moro,[a,b] Stefano Liberi,[a] Elise Daems,[b,c] Sonia Covaceuszach,[d] Alberto Cassetta,[d] Alessandro Angelini,[a] Karolien De Wael,[b] Ligia M. Moretto[a]

[a] *Department of Molecular Science and Nanosystems, Università Ca' Foscari, Mestre, Italy*
[b] *AXES Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium*
[c] *BAMS Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium*
[d] *Istituto di Cristallografia–CNR, Trieste Outstation, Trieste, Italy*
giulia.moro@unive.it

A better understanding of the interactions between perfluroocatanoic acid (PFOA) and human serum albumin (HSA) can improve the design of protein-based electrochemical biosensors for fluorinated environmental contaminants, namely per- and poly-fluoroalkyl substances (PFAS). In the last decade, the affinity of PFOA for fatted and defatted serum albumin was confirmed by numerous toxicological studies.[1-3] The results showed that PFOA can bind strongly to serum albumins, such as HSA, mimicking fatty acids binding and affecting the functions of these transport proteins. To transpose these findings in the design of bioreceptors, a multi-analytical study was carried out comparing directly the performances of fatted and defatted HSA in terms of stability, number of binding sites and affinity towards PFOA and other PFAS . Isothermal titration calorimetry (ITC) measurements allowed to define the stoichiometry and the affinity constants, while native nano-electronspray ionization MS (nESI-MS) provided additional information about the stability of the proteins and the protein-target complex. To identify the binding site and discriminate between fatted and defatted HSA, vapor diffusion crystallization was performed. All analysis confirmed the higher affinity of PFOA for the defatted HSA even though the fatted HSA showed an higher stability. Both types of HSA were immobilized on the graphite-screen printed electrodes[4] modified with graphene oxide (GO) or electropolymerized o-phenylene diamine (oPD). Impedance electrochemical spectroscopy (EIS) and cyclic voltammetry (CV) were used to characterize the immobilization strategies performances. Also direct detection by EIS and indirect detection using a redox mediator were compared to evaluate the binding event between PFOA and HSA. The combination of toxicological data and electrochemistry allowed to devise a new detection strategy for environmental contaminants, mimicking a biological process happening *in vivo* for biosensing purposes.

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P30. Hangman Effect on the Electrocatalytic Activity of an Electropolymerized Iron Porphyrin

Bettina Neumann,[a] Robert Götz,[b] Pierre Wrzolek,[c] Frieder W. Scheller,[a] Inez M. Weidinger,[b] Matthias Schwalbe,[c] Ulla Wollenberger[a]

[a] *Universität Potsdam, Institute for Biochemistry and Biology, Potsdam, Germany*
[b] *Technische Universität Dresden, Dept. of Chemistry and Food Chemistry, Dresden, Germany*
[c] *Humboldt-Universität zu Berlin, Institute for Chemistry, Berlin, Germany*
bettina.neumann@uni-potsdam.de

Synthetic or semi-synthetic analogs of enzymes are of high interest for various fields of research including bioanalysis, biosensors and chemical synthesis. A simplified design of complex structures can be useful to get further insights into the mechanism of a catalytic reaction and can imply beneficial properties such as higher stability, easier production or commercial availability. Furthermore, the reduction of the catalyst size and functional groups allows its deposition in high surface concentrations and analyses in organic solvents.

In this work, we investigated the electrocatalytic activity of the two thienyl-substituted iron porphyrins FeT3ThP and FeH3ThP (Fig. 1). In contrast to FeT3ThP, the Hangman porphyrin FeH3ThP further contained a carboxylic acid hanging group in the second coordination sphere of the iron center thereby approaching the structure of the active site of natural heme enzymes. Polymer films incorporating the porphyrins as catalytic units were deposited on glassy carbon via electropolymerization using 3,4-ethylenedioxythiophene (EDOT) as linker monomer. Scanning electron microscopy and Resonance Raman measurements demonstrated the formation of dense polymer networks incorporating the porphyrin units. The electrocatalytic reduction of molecular oxygen and hydrogen peroxide by the polymer films was analyzed using linear sweep voltammetry. Although solubility of the porphyrin monomers was restricted to organic solvents, catalysis could be demonstrated in aqueous solution. Both, FeT3ThP/PEDOT and FeH3ThP/PEDOT, catalyzed the four-electron-reduction of molecular oxygen to water with onset potentials around +0.14 V vs. Ag/AgCl (aqueous solution, pH 7). However, significant differences were obtained for the reduction of hydrogen peroxide. Compared to FeT3ThP/PEDOT films, FeH3ThP/PEDOT showed with +0.33 V vs. Ag/AgCl a 50 mV more positive onset potential as well as a three times enhanced current generation at +0.2 V. Thus, the presence of the carboxylic acid hanging group enhanced the formation of a high-potential reaction intermediate, as observed for natural peroxidases.[1] For the first time, the Hangman effect was demonstrated for iron porphyrins immobilized via electropolymerization.[2]

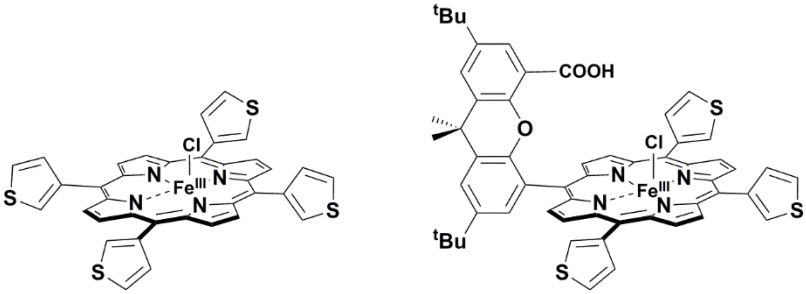

Figure 1. Structures of the thienyl-substituted iron porphyrins FeT3ThP and FeH3ThP.

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P31. Optimization of the Detection of Phenolic Compounds by Singlet Oxygen Based Electrosensing

Liselotte Neven,[a] Hanan Barich,[a] Vincent H. Y. Ching,[b] Sabine Van Doorslaer,[b] Karolien De Wael[a]

[a] *AXES Research Group, Faculty of Science, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium.*
[b] *BIMEF Research Group, Faculty of Science, University of Antwerp, Universiteitsplein 1,2610 Wilrijk, Belgium.*
liselotte.neven@uantwerpen.be

Enzymes have been used in chemical analysis for decades with horseradish peroxidase as a well-known example. Their catalytic conversion of substrates into products leads to an increased sensitivity and low detection limits. Despite this advantage, there are some challenges remaining for these sensors such as the poor stability of the enzyme and the need for additional reagents.

Therefore, we propose the use of a bioinspired photo-electrochemical sensor for the detection of phenolic contaminants. It uses a photosensitizer type II which generates singlet oxygen upon light illumination (Figure 1). The catalytic conversion of phenolic compounds, mediated by singlet oxygen, leads to an improved sensitivity and low detection limits (nM-level).[1,2] However, a profound analysis and optimization of this detection strategy has not yet been performed.

The production of singlet oxygen between different phthalocyanine derivatives is compared by using singlet oxygen probes e.g. TEMP for EPR detection or 9,10-dimethylanthracene (DMA) for UV-Vis detection. The optimum photosensitizer is deposited on a TiO_2 matrix and dropcasted on graphite screen-printed electrodes. A comparison between different photosensitizer loadings showed that 3wt% photosensitizer loadings are optimal when measuring concentrations of phenols in the nM-range.

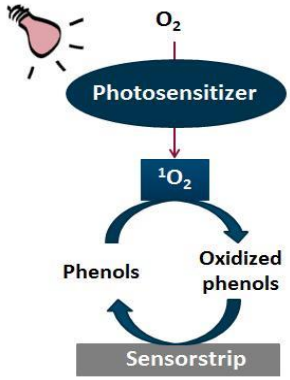

Figure 1. Mechanism of singlet oxygen based electrosensing.

To demonstrate the use of the proposed photo-electrochemical sensor, the detection of phenol is optimized in terms of pH and applied potential. The obtained detection limit of 7 nM for phenol demonstrates the improved sensitivity of the sensor. However, comparing to structurally related compounds, an increased sensitivity is observed for hydroquinone and bisphenol A presumably due to their structural differences leading to different oxidation kinetics by singlet oxygen and reduction kinetics at the electrode surface.

At last, the amount of phenol in industrial samples is measured by the sensor. It is observed that challenges in the application of the sensor can arise due to the contribution of all phenolic compounds to the photocurrent of phenol.

The singlet oxygen based electrosensing strategy seems to be a valuable tool in the detection of phenolic contaminants. The sensing strategy has a high sensitivity and is more robust than enzymatic strategies without the need of additional reagents.

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P32.

Optical Sensing of Metal Ions by Sol-Gel Based Plasmonic Nanostructures

M. Oggianu,[a] C. Figus,[b] S. Ashoka Sahadevan,[a] M. Saba,[b] A. Mura,[b] G. Bongiovanni,[b] V. Lippolis,[a] C. Caltagirone,[a] F. Quochi,[b] M. L. Mercuri[a]

[a]*Dipartimento di Scienze Chimiche e Geologiche, Università degli Studi di Cagliari, I-09042 Monserrato (Cagliari), Italy*
[b]*Dipartimento di Fisica, Università degli Studi di Cagliari, I-09042 Monserrato (Cagliari), Italy*
mariangela.oggianu@unica.it

The potential of plasmonics can be exploited in the field of nanostructured devices for sensing and environmental applications. Sensing requires chemically stable and optically tunable dielectric platforms, which should be properly functionalized by using molecular compounds, as fluorophores, able to recognize different analytes, particularly heavy metal ions. In the present work we have developed an innovative sol-gel composite system (Figure 1) where Fluorescein Isothiocyanate (FITC) has been grafted on the plasmonic and silicon surfaces.

The sol-gel method was used and optimized to control the thickness of silica layers on plasmonic surfaces.[1] The silica layers were functionalized with 3-aminopropyltriethoxysilane (APTES) as linker to graft FITC on plasmonic nanostructures forming a stable and covalent bond. The resulting films were characterized via atomic force microscopy (AFM) and contact angle to check the thickness and the surface wettability.[3] The plasmonic platforms were investigated to verify luminescence and sensing properties by using different metal cations.

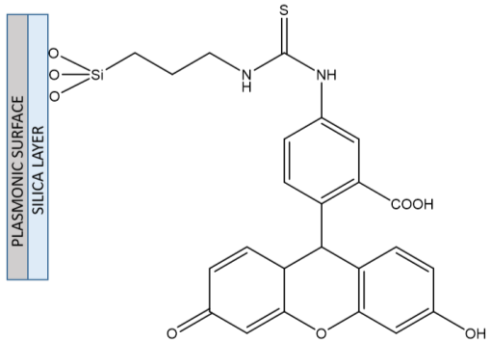

Figure 1. Sol-gel composite system

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P33. Discrimination of the Glycan Isomers 2,3-Sialyllactose and 2,6-Sialyllactose Modified with Osmium(VI) Complexes by Square Wave Voltammetry

Veronika Ostatná, Mojmír Trefulka, Hana Černocká

Institute of Biophysics, The Czech Academy of Science, v.v.i., Královopolská 135, 61265, Brno, Czech Republic
ostatna@ibp.cz

Carbohydrate components in glycoproteins play a critical role in health and disease and specificity of glycoprotein biomarkers can be greatly enhanced by the analysis of their sugar components containing frequently different isomers. Altered glycosylation is a universal feature of cancer cells and certain glycans are well-known markers of tumor progression.[1] Two glycan isomers, 2,3-sialyllactose (3-SL) and 2,6-sialyllactose (6-SL) frequently appear in glycoproteins connected with cancer. For example, various changes in the well-known Prostate Specific Antigen (PSA) glycosylation were found at cancer patients, including the increased amount of 3-SL. We combine glycan modification with osmium(VI) N,N,N',N'-tetramethylethylenediamine (Os(VI)tem) and square wave voltammetry for discrimination of 3-SL and 6-SL regioisomers.[2] Covalent adducts of Os(VI)tem with glycans yielded three reduction voltammetric peaks. The ratio of peak I/peak II heights depends on the content of individual regioisomers in the sample. Experiments using capillary electrophoresis, inductively coupled plasma mass spectrometry and thin layer chromatography showed that 6-SL molecule can bind three Os(VI), while the 3-SL only two Os(VI) moieties. A similar pattern of Os(VI)-modification was found for isomers of sialyl-N-acetyllactosamine and sialylgalactose.[3] Our proposed approach allows the determination of isomer percentage representation in the mixture after one voltammogram recording. These results show a new appropriate method for the discrimination of glycan isomers containing terminal sialic acid important for distinguishing between cancerous and non-cancerous origin of biomarkers. We can conclude that the electrochemical analysis appeared suitable for the recognition of SL isomers.

Acknowledgements:
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P34. Label Free Electrochemical Immunosensing Platforms Based on Self-Assembled Monolayers for Monitoring of Aβ$_{1-42}$ Fibrils

Gopal Palla, Jerzy Radecki, Hanna Radecka

Institute of Animal Reproduction and Food Research, Polish Academy of Sciences, Tuwima Str. 10, 10-748, Olsztyn, Poland,
palla.gopal@pan.olsztyn.pl

Beta-Amyloid formation and its further polymerization into oligomers and fibrils, is one of the key responsible factors for the damage of neurons, which leading to the Alzheimer's disease (AD).[1,2] Still, proper treatment is not available.[3] Therefore, early AD detection and prevention are the most important concerns of researchers.

Herein, two types of immunosensors monitoring of Aβ$_{1-42}$-fibrils. Anti-Amyloid Fibrils OC antibodies (MILLIPORE Cat. # AB2286) ensured their selectivity. The time required for the immobilization of OC antibodies on the sensing surfaces as well as time for OC - Aβ$_{1-42}$-fibrils interactions were estimated by using Surface Plasmon Resonance (SPR).

The monolayers self-assembled on the gold electrode incorporated transition metal complexes can act both as receptor ("host") immobilization sites, as well as transducer for interface recognitions of "guest" molecules present in the aqueous solutions. Thus, there is no need to use the redox marker in the sample solution.[4] This analytical approach was applied for electrochemical sensing of Aβ$_{1-42}$-fibrils (Scheme A). The whole OC antibodies were attached to terpyridine-Cu(II)-terpyridine-NHS complex via creation of amide bonds. The interface interactions between OC and fibrils were tracking by changes of Cu(II)/Cu(I) redox current measured with Square Wave Voltammetry (SWV). Another sensing approach was based on AuNPs covalently attached to 4,4'-Thiobisbenzenethiol (TBBT) self- assembled on the electrode surface.[5] AuNPs ayers was very suitable for covalent immobilization of F_{ab} part of antibodies having *disulfide* groups[6] (Scheme B). The interactions between OC and fibrils were tracking by changes of the charge transfer resistance measured with Electrochemical Impedance Spectroscopy (EIS) in the presence of $[Fe(CN)_6]^{-3/-4}$ redox marker. The sensing of Aβ$_{1-42}$-fibrils were performed in buffer solution (PBS) and artificial cerebral fluids. Finally, biosensors selectivity were confirmed in the presence of Aβ$_{1-42}$-oligomers.

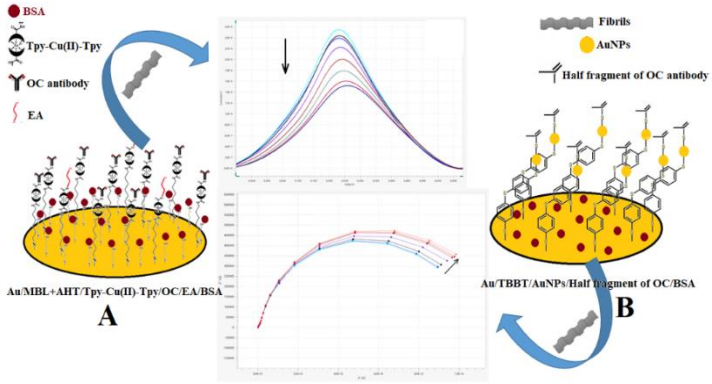

Fig. 1 Schematic illustration of immunosensors: A-based on Tpy-Cu(II)-Tpy redox active monolayer, B-based on TBBT- AuNPs SAM (redox marker $[Fe(CN)6]^{-3/-4}$ is present in the sample solution).

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P35. Two-photon Stereolithography for the Direct Writing of 3D MIP Photonic Crystals

Ernesto Paruli, Carlo Gonzato, Karsten Haupt

Génie Enzymatique et Cellulaire, Sorbonne Universités, Université de Technologie de Compiègne, CNRS Laboratory for Enzyme and Cell Engineering UMR 7025, 60200 Compiègne, France
ernesto-3.paruli@utc.fr

Two-photon stereolithography (TPS) has gained an increasing interest as a rapid prototyping technique for 3D micro- and nanostructures.[1] Due to the high energy densities required by the two-photon absorption process, it is possible to spatially confine the polymerization of a photoresist into the very small volume represented by the focal point of a microscope's objective using a pulsed laser. This allows in turn for the **direct** and **precise** fabrication of micro-/nano-structures, conversely to conventional microstereolithography.[2] In this study, TPS has been exploited for the direct fabrication of photonic crystals, which were molecularly imprinted against propranolol as a model template. Molecularly imprinted polymers (MIPs), which are also known as plastic antibodies[3] are polymers able to specifically recognize a target molecule and as such, they are well suited as recognition elements for sensors.

Thus, TPS was successfully used for the one-step synthesis of an optical sensor, including both a transducer (i.e. the photonic crystal) and a recognition element (i.e. the MIP), in a single structure.

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P36. Silanization of Spherically-shaped WGM Resonators for Cancer Detection

Piotr Paszke,[a] Rafał Nowaczyński,[a,b] Kamil Szlachetko,[a] Andrea Csaki,[c] Dorota Anna Pawlak[a,d]

[a] *Faculty of Chemistry, University of Warsaw, ul. Ludwika Pasteura 1, 02-093 Warsaw, Poland,*
[b] *Faculty of Materials Science and Engineering, Warsaw University of Technology, Wołoska 141 St., 02-507 Warsaw, Poland*
[c] *Leibniz Institute of Photonic Technology (IPHT) Jena, Member of the Leibniz Research Alliance - Leibniz Health Technologies, Albert-Einstein-Straße 9, 07745 Jena, Germany*
[d] *Institute of Electronic Materials Technology, Wólczyńska 133, 01-919 Warsaw, Poland*
ppaszke@chem.uw.edu.pl

Whispering gallery mode (WGM) optical resonators can be used for many applications, such as optical switches, narrow band lasers or thermo- and biosensors.[1,2] Particularly interesting is the application of that resonators in biosensing, due to the significantly enhanced light-matter interactions.

The aim of our work is to prepare the WGM resonators, which can be used to detect exosomes. Exosomes are small vesicles which are excreted by every cell in our body to body fluids (for ex. blood and urine). By detecting exosomes from cancerous cells we want to perform fast, early and non-invasive cancer diagnostics.

We develop WGM microresonators from fused silica and also from low-melting materials (like tellurite and phosphate glasses). For our current knowledge, we developed for the first time the resonators, based on phosphate and tellurite glasses doped with both quantum dots and plasmonic nanoparticles. We have achieved this through using the NanoParticle Direct Doping method,[3] which is based on one of the crystal growth techniques - the micro-pulling down method.

The next stage of our work is to cover the resonators with a biologically active material, that will allow us to specifically bind to tumor exosomes. The glass silanization procedure was used to functionalize the surface, allowing the glass to be coated with the antibodies that capture target exosomes. We performed functionalizations of WGM resonators with the use of GOPS (3-Glycidyloxypropyltrimethoxysilane) silanes based on works by Moller et al.[4] To verify surface coverage by silanes, silanized samples were placed in a solution of fluorescent oligonucleotide. This work presents the results of silanization tests of WGM microresonators from various types of glasses.

Acknowledgments:
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P37.

Research on Novel Matrix Composites Based on Reduced Graphene Oxide for Electrochemical Sensor Construction

Aleksandra Pollap, Karolina Waląg, Jolanta Kochana

Jagiellonian University, Kraków, Poland
aleksandra.pollap@gmail.com

Chromatographic and spectroscopic methods belong to the most popular analytical methods. Their application allows to carry out both qualitative and quantitative analyzes with high accuracy and precision. Nevertheless, application of these methods is often related with high cost of apparatus and need for special sample preparation. Therefore, it is worth to note the electroanalytical methods including electrochemical sensors and biosensors. Their use meets the requirements of analytical procedures, such as simplicity and speed of determination, accuracy, precision and low detection limit. Modification of electrode surface is an important issue during electrochemical sensor construction. The main goal of surface modification is to increase the active area, increase of electrical conductivity as well as improvement of sensor durability. Consequently, the modification of electrode surface allows to improve analytical parameters of developed sensor such as sensitivity, limit of detection or selectivity. The purpose of presented work was to carry out the research on novel matrix composites based on reduced graphene oxide (rGO). Due to structural flexibility and electrical conductivity rGO is a very attractive material.[1] In presented work rGO was used for modification of graphite electrode surface. During sensor construction titatnia dioxide sol as binding agent was used. Additionaly, the matrix composite was also enriched with gold nanoparticles increasing the electrical conductivity and conductive polymer – Nafion increasing the stability of sensor indication. The experiments were carried out in Fe(II)/Fe(III) redox probe, applying cyclic voltammetry techinque. Obtained results enabled to indicate the optimal composition of matrix nanocomposite which will be verified for sensor development for determination of pesticides.

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P38. **Electrochemical Molecularly Imprinted Polymer (MIP) Sensor for Novel Psychoactive Substances**

Rosa A.S. Couto,[a] Séfora S. Costa,[a] João G. Pacheco,[b] Cristina Delerue-Matos,[b] Eduarda Fernandes,[a] Félix Carvalho,[c] Luís M. Gonçalves,[d] Cecília M.P. Rodrigues,[e] M. Beatriz Quinaz[a]

[a] *LAQV, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal*
[b] *LAQV, REQUIMTE, Instituto Superior de Engenharia do Porto (ISEP), Politécnico do Porto, Porto, Portugal*
[c] *UCIBIO, REQUIMTE, Laboratory of Applied Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal*
[d] *Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo (USP), São Paulo, Brazil*
[e] *Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal*
bquinaz@ff.up.pt

In this work we propose an electrochemical molecularly imprinted polymer (e-MIP) to the selective quantification of the psychoactive substance 3,4-methylenedioxymethamphetamine (MDMA), also known as ecstasy (Fig. 1), using screen-printed carbon electrodes (SPCEs).[1] The device was constructed using *ortho*-phenylenediamine (*o*-PD) as the MIP's building monomer and MDMA as template. The step-by-step construction of the SPCE- MIP sensor was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The proposed electrochemical sensor worked by directly measuring the MDMA oxidation signal through square-wave voltammetry (SWV) after an incubation period of 10 min. Several parameters that could influence the sensor' sensing performance were optimized, such as the monomer/template ratio, the number of electropolymerization scanning cycles, and the incubation period. Under optimized conditions, the sensor exhibited suitable selectivity, repeatability, reproducibility and up to one month of stable response, with a linear range up to 0.2 mmol L^{-1}. Finally, the developed sensor was successfully applied to human blood serum and urine samples, showing its potential for application in medicine and in forensic sciences.

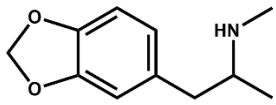

Figure 1. Structural formula of ecstasy.

Acknowledgements:
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P39. **Strategies for Aligning Silver Nanowires for Biosensing**

Heman Kumar Ramiya Ramesh Babu,[a] Joanna Niedziółka-Jönsson,[a] Sebastian Maćkowski[b]

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

[b] *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, 5th Grudziadzka St., 87-100, Toruń, Poland*

hkumar@ichf.edu.pl; jniedziolka@ichf.edu.pl; mackowski@fizyka.umk.pl

Biosensors constructed with nanomaterials have shown high sensitivity, rapid performance and low sample consumption. One-dimensional nanomaterials such as metallic nanowires are renowned for their optical and electronic properties: they can either quench or enhance the fluorescence intensity, depending predominantly on their separation from fluorophores, they can facilitate energy propagation, and last but not least, can be directly imaged with a microscope. These unique properties of metallic nanowires have been exploited in developing biosensors[1,2]. However, the spatial alignment and immobilization of nanowires to surfaces is rather challenging as this aspect is critical for fabrication of sophisticated biosensing platforms. In this work, we have explored various strategies for alignment and immobilization of nanowires at predefined locations and in a reproducible fashion. Our approach involves combination of surface modification with silanes and immobilizing cysteamine modified silver nanowires. Initially, we exploited the capillary forces to align the nanowires within peel-able microchannel set up. We observed the nanowires readily aligned in the direction of the flow and are attached to the silane patterns created with PDMS stamps. The degree of alignment was quantified using image processing software.

Fig. 1 (A) PDMS stamp, (B) Stamped silane patterns, (C) Aligned and immobilized silver nanowires.

Acknowledgements:
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P40. Different Redox Probes for Electrochemistry at the Three-phase Junction

Vishwanath R. S, Emilia Witkowska-Nery, Martin Jönsson-Niedziółka

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, ul. Kasprzaka 44/52, Poland

vishwanath.r.s@ichf.edu.pl

The three-phase electrode (TPE) ion transfer studies at organic/aqueous/electrode interface are essential to obtain highly important thermodynamic data which determine the lipophilicity, biological and pharmacological activity of transferring ions/compounds. Also, lipophilic/hydrophilic interface created at TPE is the simple model of complex biological systems. In TPE configuration, the electron transfer across the electrode/organic interface is accompanied by the ion transfer from aqueous to organic phase, which allows to determine the lipophilicity of a large number of inorganic and organic ions in different liquid/liquid interfaces.[1]

For cations transfer studies, iodine[2] and iron(III) tetraphenyl porphyrine chloride[3] have been used so far. We investigated the reduction of 1-aminoanthraquinone (AQ), and 2,3-dichloro-1,4-naphthoquinone (NQ) at a three-phase junction formed by n-octyl-2-pyrrolidone/aqueous electrolyte/glassy carbon (GC) working electrode. The redox behaviour of AQ (in anthracycline drugs) and NQ (in vitamin K) play a significant role in the biochemistry of living systems. AQ underwent a 1-step, 2-electron reduction resulting in the transfer of cations from the aqueous phase. NQ reduction occurred in two steps, the first was by a transfer of the $NQ^{\bullet-}$ radical to the interface with the reduction potential dependent on the anion present in the aqueous phase due to salting-out effects. After that, the $NQ^{\bullet-}$ radical was reduced to NQ^{2-} dianion resulted in a transfer of cations from the aqueous phase.[4] Importantly, the cation transfer potential is determined by ion-pair formation with the quinone, rather than the solvation energy of cation in the pure organic solvent.[3]

Decamethylferrocene has been extensively used for anion transfer studies so far. We synthesised a mononuclear lipophilic ruthenium(II) complex $[Ru(LR)(L)]^0$ having tridentate 2,6-bis(1-(2-octyldodecan)benzimidazol-2-yl)pyridine (LR) and (2,6-bis(benzimidazol-2-yl)pyridine) (L) ligands. Further $[Ru(LR)(L)]^0$ complex was used as a redox probe for the anion transfer studies at nitrobenzene/aqueous/GC working electrode three-phase interface. The metal associated the oxidation of $[Ru(LR)(L)]^0$ complex is accompanied by the anion transfer from the aqueous to the organic phase. The formal oxidation potential of $[Ru(LR)(L)]^0$ depends on the hydrophilicity of the aqueous anion and its concentration. The prime requirement for anion transfer is the oxidation of $[Ru(LR)(L)]^0$ complex at TPE before the water oxidation at GC/water interface which was achieved by the deprotonation at N-H sites of L ligand. Further, the deprotonated sites allow us to examine any proton coupled anion transfer from aqueous to organic phase.

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P41. Zinc Complex Mediated Phosphate Sensing via Self Assembled Monolayer Modified Gold Electrodes

Unni Sivasankaran,[a] Lena Reinke,[b] Sanu K. Ananad,[c] Stefan Kubik,[b] Krishnapillai Girish Kumar,[c] Hanna Radecka,[a] Jerzy Radecki[a]

[a] *Department of Biosensors, Institute of Animal Reproduction And Food Research of The Polish Academy of Sciences, ul. Tuwima 10, 10-748 Olsztyn, Poland*
[b] *Technische Universität Kaiserslautern, Fachbereich Chemie - Organische Chemie, Erwin-Schrödinger-Straße, 67663 Kaiserslautern, Germany*
[c] *Department of Applied Chemistry, Cochin University of Science and Technology, 682 022, Kochi, India*
unni.sivasankaran@pan.olsztyn.pl

The recognition of anions in water is a challenging area of research. Compared to the design of cation receptors, the development of anion receptors is more difficult due to the special properties of anions such as more widely differing structures, their varying protonation states at different pH and low charge to radius ratios.[1,2] A number of anion receptors are available nowadays that allow the selective binding of anionic species in water.[3,4] Our group is actively involved in the development of anion sensors. The selective sensing of sulfate over other anions was achieved recently by using electrodes with immobilized anion-binding cyclopeptides.[5] As a continuation to our works on anion sensors, the present work is devoted to the development of a new voltammetric method for the precise measurement of phosphate ions in environmental samples. A two-stage modification procedure was used to prepare self-assembled monolayers on a gold surface by using a mixture of 4-mercapto-1-butanol and a lipoic acid derivative with a zinc-dipicolylamine moiety as the anion recognition motif. Under optimized conditions, the determination of phosphate at femtomolar concentrations could be achieved with this sensor without an external redox marker in a sample solution. The preparation and application of this sensor is shown Figure 1. In order to validate the utility of developed sensor in environmental monitoring, estimation of the phosphate content in lake water sample was carried out and the results were satisfactory.

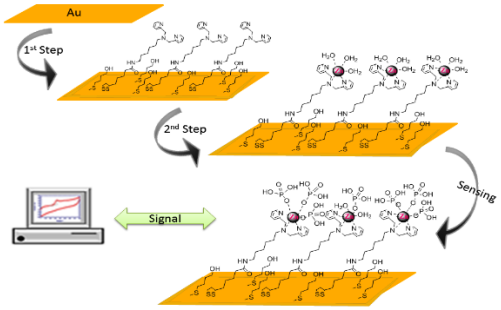

Figure 1. Modification of gold electrode and sensing of phosphate.

Acknowledgements:
This work was supported by project: National Science Centre, Poland, No-2016/21/B/ST4/03834. Financial support from the Deutsche Forschungsgemeinschaft (KU- 925/10-1) and India-Polish Inter-governmental Science and Technology Cooperation Programme 2016-2018 are also gratefully acknowledged.

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P42. Oscillatory Behaviour and Memory Effect in Cellular Automaton Simulations of Metal Passivation

Jan Stępień,[a] Janusz Stafiej[b]

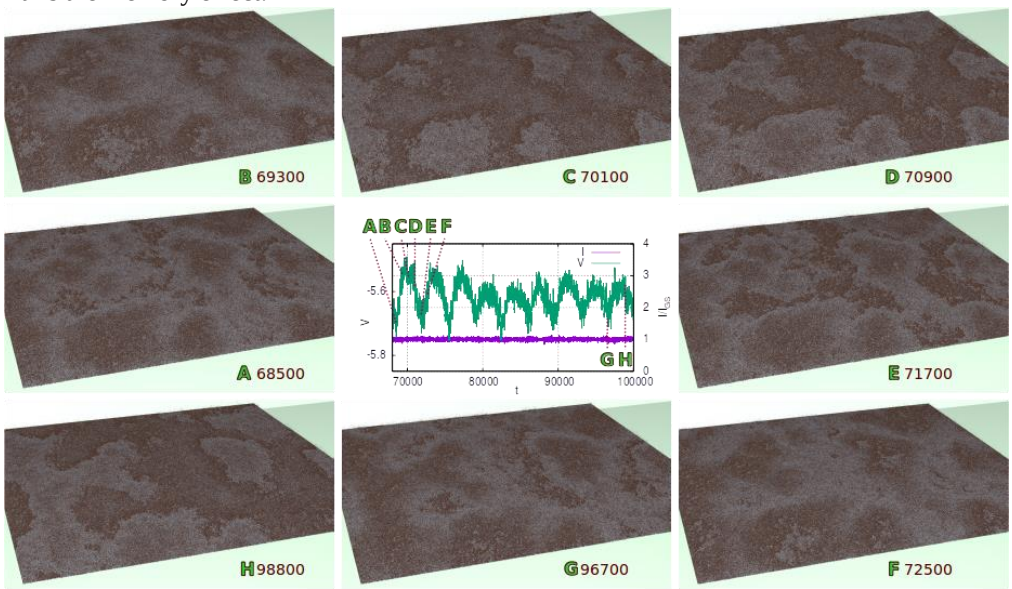
[a] *Department of Complex Systems and Chemical Information Processing, Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland*
[b] *Cardinal Stefan Wyszyński University, Faculty of Mathematics and Natural Sciences – School of Exact Sciences, ul. Wóycickiego 1/3, Warsaw, Poland*
jstepien@ichf.edu.pl

Depending on the conditions, corrosion products on metal surface may form a layer, inhibiting further corrosion. The process is called passivation.[1] Corrosion experiments are conducted on metals immersed in electrolyte solutions, in current-controlled or potential-controlled regime.[2] In such experiments, oscillations of potential *V* and of current *I*, respectively, have been observed.

Our research involves computer simulations of corrosion/passivation of a metal electrode in electrolyte under either galvanostatic or potentiostatic control. We use a simple 3D stochastic cellular automaton (discrete lattice system). The key phenomena included in the model are metal oxidation and reshaping of the oxide layer – by dissolution, diffusion and adsorption. The model is as general as possible, without assuming a specific metal or solution composition.[3]

Despite the model simplicity, we have obtained both *I* and *V* oscillations. We have also observed interesting patterns formed by the oxide on the metal surface. The surface morphology usually changes along with the phase of *V* or *I* oscillations.

An example of *V* oscillations in galvanostatic regime is shown on the figure. The plot shows the potential *V* (in green) as it changes with time (*V*, *I* and *t* in arbitrary units). The surrounding pictures show surface morphology (metal – gray, oxide – brown) in the selected moments of time. The pattern sharpens and blurs repeatedly. It reappears with very little changes after several oscillations – compare **A** with **G** or **D** with **H**. We call this the memory effect.



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P43. **Real-time Sensing with Elongated Silver Nanoparticles**

Karolina Sulowska,[a] Ewa Różniecka,[b] Kamil Wiwatowski,[a]
Joanna Niedziółka-Jönsson,[b] Sebastian Maćkowski[a,c]

[a] *Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland*
[c] *Baltic Institute of Technology, Gdynia, Poland*
sulowska@fizyka.umk.pl

In this work we focus on applying silver nanowires (AgNWs) as building blocks of a biosensor. The nanowires feature several key properties that make them suitable for this application,[1-3] which include chemical stability in water and buffer solutions, straightforward synthesis using wet chemistry, as well as ability to control the functionality via appropriate surface modifications. Importantly, the diameters of the nanowires, which are around 100 nm and their lengths of around 50 μm, facilitate plasmon resonance and ability to visualize the nanowires using optical microscopy, respectively.

We tested the sensor ability of the nanowires using natural photosynthetic complexes, Peridinin-Chlorophyll-Protein (PCP) modified with streptavidin. The size of the PCP complex is 4 nm, i.e. much less than typical diameters of AgNWs. The absorption and fluorescence spectra of PCP overlap with the extinction spectrum of AgNWs, facilitating plasmon coupling.[4] The experiments were carried out using advanced fluorescence microscopy and spectroscopy techniques.

Upon modification of the AgNWs surface with biotin, we placed them on a surface. In the next step a droplet of PCP solution was deposited and fluorescence of an area of 100 x 100 microns was monitored in real-time mode. We observe specific attachment of the PCP complexes to AgNWs. Importantly, with this approach we can demonstrate detection of single proteins in real-time. Partially this is due to plasmonic enhancement of PCP emission, as evidenced by time-resolved fluorescence microscopy. In addition to this approach, other ways of improving the efficiency of the detection or the limit of detection will be presented.

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P44. Investigation on Selectivity of Blood Vancomycin Sensor Using Molecularly Imprinted Polymer Carbon Paste Electrode

Yuuto Takeda,[a] Yasuo Yoshimi,[a] Akihiko Hatano[b]

[a] *Department of Applied Chemistry, Shibaura Institute of Technology, 3-7-5, Toyosu, Koto-ku, Tokyo 135-8548, Japan*
[b] *Department of Material Engineering, Shibaura Institute of Technology, 307 Fukasaku, Minuma-ku, Saitama City, Saitama 337-8570, Japan*
yosimi@sic.shibaura-it.ac.jp

Vancomycin(VCM) is the drug of first choice for treating Methicillin-Resistant Staphylococcus Aureus (MRSA) infections which is the main causative bacteria of nosocomial infection. Therapeutic drug monitoring (TDM) of VCM is strongly recommended in order to prevent side effect and creation of the resistant bacteria. However, TDM does not work sufficiently, because frequent measurement of blood level of VCM is still difficult. We are developing a blood-VCM sensor with a paste electrode of graphite particle on which a molecularly imprinted polymer (MIP) is immobilized covalently in this study.

Graphite particles coated with photoinitiator of radical polymerization were dispersed in a prepolymer solution (VCM as a template material, methacrylic acid as a functional monomer, *N, N'*-methylenebisacrylamide as a crosslinking monomer, acrylamide as a crosslinking and allylamine carboxypropionic-3-ferrocene as a electoron-mediator) and irradiated with xenon lamp. The MIP carbon was mixed with silicone oil and filled in a glass tube to prepare a carbon paste electrode immobilizing MIP of VCM. The specimen was prepared by dissolving VCM or TEIC in phosphate buffer saline(PBS) or, bovine whole blood. The relationship between current obtained by differential pulse voltammetry and the concentration of VCM or TEIC was observed.

The calibration lines for VCM and TEIC (whose structure is similar to VCM with the same antibacterial agent) of MIP electrodes are compared in PBS, whole blood in **Fig. 1**. **Table 1** shows the sensitivity to each antibacterial agent in the blood or the saline. The electrodes were highly sensitive to VCM in each measurement solution. The sensitivity to TEIC was lower than VCM in PBS or the blood. The result indicate that this VCM-MIP electrode can discriminate between the VCM and TEIC whose molecular structure is similar to VCM. Therefore, the MIP electrode can sense VCM with high specificity even in blood. We can conclude that the MIP electrode is feasible for TDM of VCM, which is required for beating the resistant bacteria.

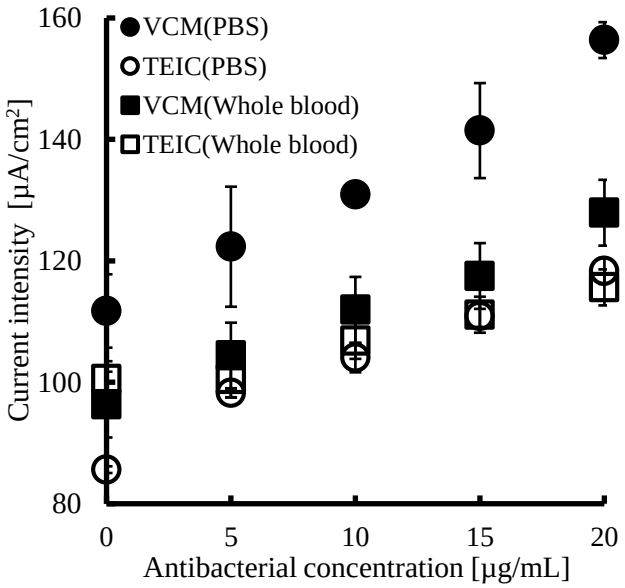

Fig. 1 Relationship current at the MIP electrode

Table 1. Sensitivity of MIP electrode in each measurement solution

Medium	Sensitivity [A・cm/g]
VCM(PBS)	2.17
TEIC(PBS)	1.56
VCM (Whole blood)	1.53
TEIC (Whole blood)	0.82

P45. Gold Thin-Film Based Photo-electrochemical Planar DNA Sensors

Saranya Thiruvottriyur Shanmugam, Stanislav Trashin, Karolien De Wael

AXES Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium
Saranya.ThiruvottriyurShanmugam@uantwerpen.be

Gold-sputtered three-electrode planar structures have recently become commercially available as an attractive platform for development of cost-efficient and disposable biosensors. However, critical aspects such as preparation and characterization of the gold surface, evaluation of immobilized DNA probes onto gold substrates and control of their reproducibility are often dismissed, though these parameters directly affect the characteristics of the sensor.

In the current work, we evaluated the applicability of commercially available sputtered thin-film gold electrode structures that consist of three planar gold electrodes and can be used for the analysis in a drop of few microliters. These electrodes were characterized in comparison to gold disk electrodes that are typically used as a model support for DNA sensors. Three surface pretreatment methods were compared and the optimal non-tedious pre-treatment procedure using a drop cell connector was chosen. Different methods including electrochemical approaches for immobilizing oligonucleotide probes on the gold surface were performed with the aim to minimize/eliminate non-specific adsorption of the oligonucleotides on the gold, creating a better-defined electrode surface. Surface densities of the immobilized probes through different approaches were determined using chronocoulometry with ruthenium hexamine. Furthermore, electrodes with single thiolated probes immobilized by both methods were further evaluated for their ability to capture the complementary target ssDNA and the detection strategy was based on alkaline phosphatase based enzymatic assay. The best strategy was chosen and adapted for photo-electrochemical detection of the DNA-DNA hybridization.[1] The detection strategy here is based on a photosensitizer type II which generates singlet oxygen under light illumination and further reduction of this singlet oxygen at the electrode surface resulting in the current response. With an intrinsic background elimination feature by switching the light ON/OFF, this photo-electrochemical strategy provides enhanced sensitivity.[1]

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P46. Photoelectrochemical Sensing of 4-Nitrophenol Based on ZnO Nanostructured Sensitized by Carboxylated Perylene

Camila D.M. Verbinnen, Sergio A.S. Machado

Institute of Chemistry of São Carlos, University of São Paulo, IQSC – USP, Av. Trabalhador São-carlense 400, São Carlos – SP, Brazil
camiladm@usp.br

A voltammetric method for the quantification of 4-nitrophenol (4-NP) was proposed using a nanostructured zinc oxide (ZnO) sensitized by perylene-3,4,9,10-tetracarboxylic acid (PTCA), under UV light illumination. 4-NP is the main degradation product of pesticides ethyl and methyl-paration and it is also classified as a toxic compound according to U.S. Environmental Protection Agency (U.S. EPA).[1] Due to its high stability in aqueous matrix and its harmful effects to the environment, 4-NP is considered as an ordinary water pollutant.[2] Based on the hazardous nature of 4-NP the concern with public health needs accurate knowledge, in real time, of the water contamination level, as well as soil and food, with this organic pollutant. In the last years photoelectrochemical analysis has been explored, increasingly, for the analysis of toxic organic molecules. In this methodology, a semiconductor material such as ZnO is used to harvest the energy from UV or visible light and transform it into the electron/hole pair.[3] The holes and electrons can react with the available molecules adsorbed on ZnO surface, like OH^- and H_2O and generate reactive oxygen species (ROS). ROS can oxidize the target molecule allowing its quantification by the photocurrent response generated. The ZnO nanorods were synthesized by a simple electrodeposition method on the surface of fluorine-doped tin oxide (FTO) glass and the PTCA was synthesized by hydrolysis and neutralization steps. Afterwards, the PTCA was coated on the ZnO surface by drop. The prepared sensor was characterized by morphological (XRD, SEM-EDX, RAMAN), optical (UV-vís and diffuse reflectance spectroscopy (DRS)) and electrochemical techniques (chronoamperometry, linear voltammetry and EIS). The absorption coefficient of ZnO was determined by the DRS optical characterization and, therefore, the bandgap energy of 2.96 eV was calculated. The photosensitivity of the ZnO_Perylene film was evaluated by linear scanning measurements and photocurrent transient chronoamperograms in the dark and under illumination, using a black UV lamp (20 W). After characterization step and at optimum conditions the photosensor was used to quantify 4-NP. The strategy of PTCA and ZnO interaction enhanced significatively the photocurrent response. Linear calibration curve was obtained on the range 0.1 – 15 $nmolL^{-1}$ in a phosphate buffer solution 0.01 $molL^{-1}$ pH 7.1, with limit of detection (LOD) 0.09 $nmolL^{-1}$. The ZnO nanorods on FTO surface were obtained using a simple and fast electrodeposition synthesis and its combination with PTCA were successful optimized. A sensitive low cost photosensor was developed with the possibility of application "in situ" and in real-time for the quantification of 4-NP.

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P47. A Detection Scheme for the Quasi-continuous Monitoring of Biomarkers

Tobias Vöpel,[a] Lukas Straczek,[b] Jürgen Oehm,[b] Nicolas Plumeré[a]

[a] *Center for Electrochemical Sciences, Ruhr University Bochum, Germany*
[b] *Faculty of Electrical Engineering and Information Technology, Ruhr University Bochum, Germany*
tobias.voepel@rub.de

Testing of vital biomarkers is becoming increasingly important in clinical analysis. Usually, immunoassays such as ELISA (Enzyme-linked Immunosorbent Assay) are used in which detection is realized by absorption, fluorescence or luminescence. These assays are however labor-intensive and time-consuming, which is why they are usually performed in specialized laboratories and rarely as point-of-care (POC) diagnostics.[1] Electrochemical detection has the potential to establish POC immunoassays as the diagnostic method of choice.

Aim of this work is to develop an electrochemical sensor for the automated and quasi-continuous monitoring of biomarkers at the bedside. Antibodies specific to the biomarker of interest are immobilized on a gold electrode using thiol-gold bonding.[2] For the electrochemical detection of the antibody-antigen interaction EIS (Electrochemical Impedance Spectroscopy) will be used.[3] Antibodies strongly bind to their antigen upon encounter, that is why an antibody activated surface can only be used for a single binding event. To achieve a quasi-continuous detection of biomarkers in complex liquids like blood or urine we combine an array of microelectrodes with the chemical protection of the electrode surfaces with a polymer. In this detection scheme individual electrodes can be activated for a single binding event in a controlled sequence to establish monitoring of biomarkers over an extended time period. To remove the protective polymer layer, the pH will be locally lowered by electrochemical water splitting through a dedicated microelectrode in close vicinity of the detection electrode. The array of microelectrodes is fabricated using CMOS technology, with integrated automated evaluation. Data analysis is based on a new method for impedance spectroscopy, which is particularly robust with regard to noise and can be easily integrated into CMOS circuits.[4]

Integration of such an immuno-microelectrode array into a central catheter will enable monitoring of relevant biomarkers in biological liquids (blood, urine).

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P48. **Modifying Bacteria with Light-Harvesting Nanoparticles: Rational Development of Biohybrids for Solar Chemicals and Fuels**

Huijie Zhang,[a] Jessica H. van Wonderen,[b] Erwin Reisner,[c] Julea N. Butt,[b] Lars Jeuken[a]

[a] *School of Biomedical Sciences, University of Leeds,UK*
[b] *School of Chemistry and School of Biology, University of East Anglia, UK*
[c] *Department of Chemistry, University of Cambridge, UK*

Inorganic-biological hybrids which combine synthetic light-harvesting nanoparticles and biocatalysts show great potential to harvest solar energy for chemicals and fuels production in a sustainable way.[1,2] Inspired by natural photosynthesis, we aim to provide proof-of-principle for whole-cell biohybrid photocatalysis producing value-added chemicals from coupled redox transformations within Gram-negative bacterium *Shewanella oneidensis* MR-1 (MR-1). A decaheme protein complex MtrC provides a direct conduit for bidirectional electron exchange across the MR-1 outer membrane. Single point mutations were performed to prepare Cys variants of MtrC which can be selectively labelled with light-harvesting electrocatalysts at different distances to heme. The activities of redox enzymes inside Gram-negative *Shewanella* bacteria will be directly coupled to the activities of extracellular photocatalysts by rational labelling of MtrC to deliver simultaneous production of intra- and extra-cellular chemicals in closed redox cycles. This work will provide a platform to perform complex, coupled light-driven transformations in oxidation and reduction for the first time.

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P49. **Plasmonic Enhancement of mCherry Fluorescence**

Artur Ziółkowski,[a] Martyna Domagalska,[a] Karolina Sulowska,[a]
Joanna Niedziółka-Jönsson,[b] Justyna Grzelak,[a] Sebastian Maćkowski[a,c]

[a] *Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Torun, Poland*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Warszawa, Poland*
[c] *Baltic Institute of Technology, Gdynia, Poland*
291534@stud.umk.pl

In this work we study interactions between plasmonic excitations in silver nanowires and photoactive proteins. The plasmon resonance, characteristic for metallic nanoparticles[1] allows for enhancing the fluorescence emission of properly attached (bio)molecules, making the nanowires attractive structures for sensing.[2,3] In order to facilitate sensing using silver nanowires, it is critical to develop ways of specific functionalization.

The experiment was based on comparing two geometries of hybrid nanostructures composed of silver nanowires and mCherry protein, equipped with His-tag. Using fluorescence imaging and spectroscopy we evaluated plasmonic enhancement for structures, where proteins were deposited directly onto silver nanowires and where the proteins were specifically attached to them. Such differences in geometry yield changes in the fluorescence enhancement due to interactions with plasmon resonances in the nanowires. Understanding the specifics of this interaction is essential for applying silver nanowires as building-blocks of sensing devices. Additional experiments focused on proteins that can be switched by light will be presented.

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