SMCBS
2017

The 8th International Workshop on Surface Modification for Chemical and Biochemical Sensing

Programme
&
Book of Abstracts

Żelechów (near Warsaw), Poland
3 - 7 November 2017

The Bioelectrochemical Society

Aim

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

Become a Member of the BES Family!

All BES activities are organized, conducted and directed by its members.
To become a individual member, one needs to be supported by 2 members of the Society and be approved by the BES Council.

- Membership fee: **40 Euros**
- Membership fee for students: **10 Euros**

www.bioelectrochemical-soc.org

Table of content

ISBN: 978-83-939295-1-1

Acknowledgements

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

The Bioelectrochemical Society

www.bioelectrochemical-soc.org

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

office@lambdasystem.pl
www.lambdasystem.pl

Spectro-Lab
ul. Warszawska 100/102
05-092 Łomianki

tel. +48 22 675 25 67
fax. +48 22 811 98 18
info@spectro-lab.pl
www.spectro-lab.pl

Zimmer&Peacock
United Kingdom: Zimmer and
Peacock Ltd - 1 Market Hill,
Royston, SG8 9JL, United Kingdom

www.zimmerpeacock.com

Zimmer&Peacock

Zimmer & Peacock

eSensor Manufacturing and Technology

Zimmer&Peacock see that sensors are a critical part of some Social and Commercial Revolutions, including the Internet of Things (IoT), Sensor Web and the growth of the In-vitro Diagnostics Market (IVD).

At Zimmer&Peacock, we are partnering with academia and industry to ensure that there are enough suitable and commercially available sensors to meet the requirements of these new and growing markets. As part of this Zimmer&Peacock provides a range of products and services including sensors, the necessary hardware, and customer specific Android and iOS applications, IP generation and scalable manufacturing. Part of the remit at Zimmer&Peacock is to innovate around our collaborator's inventions and to help bring ideas to market.


SECM150
BioLogic
SECM150

Spectro-Lab®

Laboratoria Przyszłości

ul. Warszawska 100/102
05-092 Łomianki

tel. +48 22 675 25 67
fax. +48 22 811 98 18

info@spectro-lab.pl
www.spectro-lab.pl

Welcome

We are pleased and honored to present to you Program of the 8th International Workshop on Surface Modification for Chemical and Biochemical Sensing, SMCBS'2017. The Workshop is organized jointly by the Institute of Physical Chemistry, Polish Academy of Science, and Faculty of Mathematics and Natural Sciences, School of Sciences of the Cardinal Stefan Wyszynski University in Warsaw, Poland. In the spirit of previous workshops of this series, we are especially happy to see so 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 with us their most recent exciting results presented as keynote lectures. Moreover, we are pleased that over a dozen of scientists of international renown have accepted our invitations to deliver tutorial lectures that can be considered as inspirations for further discussions.

As previous workshops, the present one focuses on the art of both chemical and non-chemical decorating of solid surfaces. An ultimate goal of some of the research involves improvement of recognition activity of the resulting chemosensors with respect to target analytes. Main topics of the Workshop cover various aspects of surface chemistry, more or less related to chemo- and biosensing in solutions or gases, not being limited to:

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

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

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

The Organizing and Program Committee is grateful to all those who contributed to the present Workshop. We are particularly thankful to Authors of the contributions, to the persons chairing the sessions, and the members of the International Scientific Advisory Board for their excellent job accomplished in preparing scientific profile of this event.

On behalf of the Organizing and Program Committee we welcome all the participants wishing them an excellent workshop, both scientifically and socially.

Włodzimierz Kutner
Warsaw, October 2017

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.

International Scientific Advisory Board

- Renata Bilewicz (Warsaw University, Warsaw, Poland)
- Gary Blanchard (Michigan State University, East Lansing, Michigan, USA)
- Francis D'Souza (University of North Texas, Denton TX, USA)
- Lo Gorton (Lund University, Lund, Sweden)
- Karsten Haupt (Université de Technologie de Compiegne, Compiegne, France)
- Tibor Hianik (Comenius University, Bratislava, Slovakia)
- Paweł Kulesza (Warsaw University, Warsaw, Poland)
- Frank Marken (University of Bath, Bath, UK)
- Wolfgang Schuhmann (Ruhr-Universität Bochum, Bochum, Germany)
- Gunther Wittstock (Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany)

Organizing Committee

Chairperson: Włodzimierz Kutner

Members: Maria Białobłocka
Zofia Iskierko
Patrycja Łach
Kamila Łępicka
Marta Majewska
Valerii Malyshev
Paulina Materska-Wilczyńska
Ievgen Obraztsov
Piotr Pięta
Piyush Sindhu Sharma
Jyoti Yadav

SMCBS'2017

The 8th International Workshop on Surface Modification for Chemical and Biochemical Sensing

Programme & Book of Abstracts

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

Żelechów, Poland
November 3-7, 2017

SMCBS’2017 Programme

Friday, November 3

09:00-16:00		**Registration at IPC PAS**
12:00-13:00		**Lunch at IPC PAS**
13:00-19:00		**Transfer to Żelechów / Arrival**
14:00-		**Setting up posters**
19:00-20:00		**Dinner**
20:00-21:20		**Evening session** Chairs: Alexander Kuhn and Serena Arnaboldi
20:00-20:40	T01	**Frank Marken** Current Rectification and Diodes in Membrane Electrochemistry
20:40-21:00	K01	**Kamil Wojciechowski** Interaction of Biosurfactants with Lipid Membranes
21:00-21:20	K02	**Hanna Radecka** Strategies for Design of Immuno- and Genosensors-Fundamentals and Applications

Saturday, November 4

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Frank Marken and Kamil Wojciechowski
09:00-09:40	T02	**Lars J.C. Jeuken** Supramolecular Electrode Assemblies in Bioelectrochemistry
09:40-10:00	K03	**Alain Walcarius** Electrogeneration of Mesoporous Silica Films with Vertically Ordered Nanochannels for Chemical Sensing
10:00-10:15	SC01	**Pavel Zhurauski** Self-assembled Gold Nanoparticles for Impedimetric and Amperometric Detection of a Prostate Cancer Biomarker
10:15-10:30	SC02	**Fangyuan Zhao** A Solar Nernstian Biosupercapacitor Based on Cyanobacterial Photosynthetic Complexes
10:30-11:00		**Coffee break**

11:00-12:50		**Morning session 2** Chairs: Lars J. C. Jeuken and Hanna Radecka
11:00-11:40	T03	**Paweł Krysiński** Surface- and Core-Modified Nanoferrites as Tools for Magnetic Field-Assisted Targeted Drug Delivery
11:40-12:00	K04	**Tan-Phat Huynh** Precipitation of Inorganic Phases Through a Photoinduced pH Jump: from Vaterite Spheroids and Shells to ZnO Flakes and Hexagonal Plates
12:00-12:20	K05	**Barbara Jachimska** Self-assembling Behavior of Proteins: Effect of the Interaction between Protein and Surface
12:20-12:35	SC03	**Stanislav Trashin** Towards Point-of-Care diagnostic of Toxocariasis: Electrochemical and Photoelectrochemical Magnetosensor with Nanobodies
12:35-12:50	SC04	**Kamila Łępicka** A Multi-composite Supercapacitor with a Dual Anode and a Dual Cathode
13:00-14:30		**Group photo and Lunch**
14:30-16:20		**Afternoon session 1** Chairs: Paweł Krysiński and Tan-Phat Huynh
14:30-15:10	T04	**Alexander Kuhn** Chiral Recognition with Tailored Porous Metal Layers
15:10-15:30	K06	**Alessandra Maria Bossi** Molecularly Imprinted Nanomaterials Targeting Linear and Structured Peptides
15:30-15:50	K07	**Andrew James Gross** Buckypaper Bioelectrodes: Emerging Materials for Implantable and Wearable Bioelectronics Devices
15:50-16:10	K08	**Gerd-Uwe Flechsig** Structure of DNA Layers on Gold Surfaces Studied by Millisecond-resolved EQCM and H/D Kinetic Isotope Effects
16:10-16:25	SC05	**Felipe Conzuelo** Evaluation of (Bio)photocatalysts for Energy Conversion by Means of Scanning Photoelectrochemical Microscopy
16:25-17:00		**Coffee break**

17:00-18:50		**Afternoon session 2** Chairs: Alessandra M. Bossi and Trashin Stanislav
17:00-17:40	T05	**Jacek Lipkowski** Application of IR Spectroscopy to Study Thin Films of Biomolecules at the Electrified Metal-Solution Interface
17:40-18:00	K09	**Fred Lisdat** Cytochrome c as Valuable Building Block in Multilayered Architectures of Biocatalysts on Electrodes
18:00-18:20	K10	**Wolfgang Kaiser** Surface-immobilized Electrically Actuated DNA Layers for the Measurement of Binding Kinetics, Stokes Radius and Conformational Changes of Proteins
18:20-18:35	SC06	**Adam Kolodziej** Electrochemical Stability of Thiols and Disulfides Assembled on Gold in Physiological Medium
18:35-18:50	SC07	**Laurent Bouffier** Straightforward Control of Chemical Surface Gradients by Wireless Electrochemistry

19:00-20:00 Dinner

20:00-22:00 Poster session

Sunday, November 5

08:00-09:00 Breakfast

09:00-10:30		**Morning session 1** Chairs: Mathieu Etienne and Gerd-Uwe Flechsig
09:00-09:40	T06	**Karsten Haupt** Micro and Nanofabricated Molecularly Imprinted Polymers for Bioanalysis, Biosensing and Bioimaging
09:40-10:00	K11	**Piyush Sindhu Sharma** Designed Electroactive Functional Monomers for Providing Desired Selectivity in Electrochemical Molecular Imprinting
10:00-10:15	SC08	**Carlo Gonzato** Molecularly Imprinted Films on Interdigitated Electrodes via Photo-iniferter Polymerization under Visible Light
10:15-10:30	SC09	**Zofia Iskierko** Epitope Imprinting for Selective Gluten Determination

10:30-11:00 Coffee break

11:00-12:50		**Morning session 2** Chairs: Karsten Haupt and Alain Walcarius
11:00-11:40	T07	**Andrzej Lewenstam** Sensing Ion Fluxes Through Artificial and Biological Membranes and their Interfaces
11:40-12:00	K12	**Nicolas Plumere** Charge Recombination in Biophotoelectrodes
12:00-12:20	K13	**Karolien De Wael** Singlet Oxygen Based Electrosensing
12:20-12:35	SC10	**Serena Arnaboldi** Optimizing the Electrodeposition Protocol of Enantioselective Inherently Chiral Electrode Surfaces: a Multi-Technique Investigation
12:35-12:50	SC11	**Vitali Scherbahn** Wide-Field Surface Plasmon Microscopy for Detection of Biological Nano-/Microparticles
13:00-14:30		**Lunch**
14:30-15:45		**Afternoon session 1** Chairs: Andrzej Lewenstam and Karolien De Wael
14:30-14:50	K14	**Pawel Kulesza** Charge Propagation in Electroactive Materials: Diagnosis of Mechanisms and Dynamics with Microelectrochemical Devices
14:50-15:10	K15	**Gidi Shani** Sensors for Breath Testing: From Nanomaterials and Surface Modifications to Comprehensive Disease Detection
15:10-15:30	K16	**Sławomir Sęk** Activity of Lipopeptides Toward Biomimetic Lipid Films
15:30-15:45	SC12	**Mariano Garcia-Soto** Polymer-coated Gold Nanoparticles
15:45-		**Social program**
20:00-22:00		**Dinner/Banquette**

Monday, November 6, 2017

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Sławomir Sęk and Jingyuan Chen
09:00-09:40	T08	**Sergey Shleev** Biosupercapacitors
09:40-10:00	K17	**Patrizia R. Mussini** Strategies for High Enantioselectivity at Electrode Surfaces: Implementing Inherent Chirality in Electroactive Thin Films or Electrode|(Ionic Liquid) Interfaces
10:00-10:15	SC13	**Sebastian Mackowski** Wide-Field Fluorescence Microscopy of Real-time Conjugation Sensing
10:15-10:30	SC14	**Michal Kizling** Size Dependence of Gold Clusters Roles in Processes Catalyzed by Redox Enzymes
10:30-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: Sergey Shleev and Patrizia R. Mussini
11:00-11:40	T09	**Krzysztof Winkler** Formation, Characterization, and Application of 1-D Polypyrrole Structures
11:40-12:00	K18	**Mathieu Etienne** Electroactive Artificial Biofilms
12:00-12:20	K19	**Klaus Mathwig** Fluorescent and Electrochemical Sensing Confined in Nanofluidic Channels
12:20-12:35	SC15	**Maciej Cieplak** Self-reporting Molecularly Imprinted Polymer for Label-free Selective Electrochemical Sensing of *p*-Synephrine
12:35-12:50	SC16	**Roberto Ortiz** Direct Electrochemistry of Cellobiose Dehydrogenases onto Gold Nanoparticle Modified Gold Electrodes-The role of surface charges
13:00-14:30		**Lunch**
14:30-16:25		**Afternoon session 1** Chairs: Krzysztof Winkler and Sebastian Mackowski
14:30-15:10	T10	**Francis D'Souza** Artificial Photosynthesis: Surface Modified Biomimetic Materials for Light Capture, Charge Separation, and Fuel Production

15:10-15:30	K20	**Wojciech Nogala** Nanoelectrodes for Determination of Silver Species in Biological Cells
15:30-15:50	K21	**Ilaria Palchetti** Nanostructured Electrochemical Platforms for the Detection of Clinically Relevant Molecules
15:50-16:10	K22	**Munetaka Oyama** Electrochemical Characteristics of Palladium Nano- or Micro-particles Modified Electrodes
16:10-16:25	SC17	**Magdalena Michalak** Micropattering of Bare Metallic Nanostructures and their Electrocatalytic Studies in Alkaline Media. SECM pH mapping
16:25-17:00		**Coffee break**
17:00-19:10		**Afternoon session 2** Chairs: Francis D'Souza and Wojciech Nogala
17:00-17:40	T11	**Gary Blanchard** Using Ionic Liquids to Control Interface Properties over Macroscopic Distances
17:40-18:00	K23	**Camelia Bala** Versatility and Challenges in the Design of Biosensors for Food Security
18:00-18:20	K24	**Vladimir Mirsky** Detection of Nano- and Microparticles of Engineered and Biological Origin by Wide-field Surface Plasmon Microscopy
18:20-18:35	SC18	**Marcin Holdynski** Collisions of Suspended Prussian Blue Nanoparticles with Rotating Disk Electrode
18:35-18:50	SC19	**Michael Füeg** Towards Mechanistic Understanding of Silver Nanoparticle Formation Catalyzed by *Geobacter sulfurreducens*
19:00-20:00		**Dinner**
21:00-		**Disco**

Tuesday, November 7

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Vladimir Mirsky and Gary Blanchard
09:00-09:40	T12	**Ambra Giannetti** Spatially-selected Optical Microbubble Resonators for Biomolecule Immobilization
09:40-10:00	K25	**Gabriela Almeida** Construction of Electrochemical Biosensors for Nitrite Detection: Needs, Challenges and Perspectives
10:00-10:15	SC20	**Jan Hrbac** Electrode Modification by Metal-derived Nanostructures using Interelectrode Material Transfer and Spark Discharges
10:15-10:30	SC21	**Bhavana Gupta** Wireless Actuation of Conducting Polymers
10:30-11:00		**Coffee break**
11:00-12:10		**Morning session 2** Chairs: Gabriela Almeida and Ilaria Palchetti
11:00-11:40	T13	**Lo Gorton** Electrochemical Communication Between Photosynthetic Membranes/Cells and Electrodes for Harvesting Solar Energy
11:40-12:00	K26	**Jingyuan Chen** High-response Conducting Films Made of Suspensions of Polyaniline-coated Graphene
12:00-12:10		Closing
12:10-13:10		**Lunch**
13:10-		**Departures**

T01. Current Rectification and Diodes in Membrane Electrochemistry

Frank Marken

Department of Chemistry, University of Bath, Bath BA2 7AY, UK
F.Marken@bath.ac.uk

Current rectification is a well-known process in electrochemical systems where an AC input results in a DC output.[1] More recently current rectification has been found associated with nano-cone pores[2] and even with single molecule devices.[3]

This tutorial lecture will attempt to link rectification phenomena and explore in particular ionic rectification in membranes.[4] Ionic diode phenomena observed in Nafion[5] and cellulose[6] materials will be contrasted, characterization tools discussed, and future applications suggested.

References

1. S. Ciani, S. Krasne, S. Miyazaki, and S. Hagiwara *J. Membrane Biol.* **1978**, *44*, 103.
2. W. J. Lan, M.A. Edwards, L. Luo, R.T. Perera, X.J. Wu, C.R. Martin, H.S. White *Acc. Chem. Res.*, **2016**, *49*, 2605.
3. Y. Komoto, S. Fujii, M. Iwane, and M. Kiguchi *J. Mater. Chem. C* **2016**, *4*, 8842.
4. E. Madrid, Y.Y. Rong, M. Carta, N. B. McKeown, R. Malpass-Evans, G. A. Attard, T.J. Clarke, S.H. Taylor, Y.T. Long, F. Marken *Angew. Chem.-Inter. Ed*. **2014**, *53*, 10751.
5. D. P. He, E. Madrid, B. D. B. Aaronson, L. Fan, J. Doughty, K. Mathwig, A. M. Bond, N. B. McKeown, F. Marken *ACS Appl. Mater. Interf.* **2017**, *9*, 11272.
6. B. D. B. Aaronson, D. P. He, E. Madrid, M. A. Johns, J. L. Scott, L. Fan, J. Doughty, M. A. S. Kadowaki, I. Polikarpov, N. B. McKeown, F. Marken *ChemSelect*, **2017**, *2*, 871.

K01. Interaction of Biosurfactants with Lipid Membranes

Kamil Wojciechowski

Warsaw University of Technology, Faculty of Chemistry,
Noakowskiego 3, Warsaw, Poland
kamil.wojciechowski@ch.pw.edu.pl

Saponins are natural surfactants (biosurfactants) abundant in the plant kingdom. They play major role in plant's defense mechanisms thanks to their ability to interact with biological membranes. The presence of a hydrophobic aglycone (triterpenoid or steroid) and a number of hydrophilic sugar groups, render their molecules amphiphilic.[1] Consequently, many saponins exhibit not only biological activity, but are also excellent surfactants, emulsifiers, foaming agents, etc.

The molecular details of the mechanism of hemolytic and vaccine-adjuvant activity of some saponins still remain largely unknown. For many years cholesterol has been claimed the sole responsible for the affinity of saponins to mammal cell membranes. However, our recent study using model lipid mono- and bilayers shed some new light on the possible role of phospholipid components of the membrane.[2,3] In this contribution I discuss the recent developments in the study of mechanism of interaction of saponins from *Quillaja saponaria* Molina, *Hedera helix*, *Digitalis purpurea* and *Glycyrrhiza glabra* with model lipid membranes.

References

1. S.G. Sparg, M.E. Light, J.V. Staden *J. Ethnopharmacol.*, **2004**, *94*, 219.
2. K. Wojciechowski, M. Orczyk, T. Gutberlet, M. Trapp, K. Marcinkowski, T. Kobiela, T. Geue *Biochim. Biophys. Acta, Biomembr*, **2014**, *1838*, 1931.
3. K. Wojciechowski, M. Orczyk, T. Gutberlet, G. Brezesinski, T. Geue, P. Fontaine *Langmuir*, **2016**, *32*, 9064.

K02. Strategies for Design of Immuno- and Genosensors – Fundamentals and Applications

Hanna Radecka, Jerzy Radecki

Institute of Animal Reproduction and Food Research, Polish Academy of Sciences,
10-748 Olsztyn, Tuwima 10, Poland
h.radecka@pan.olsztyn.pl; j.radecki@pan.olsztyn.pl

The examples of successful developing of several type of immunosensors and genosensors destined for the detection of Highly-Pathogenic Avian Influenza type H5N1 virus (HPAI) spreading among wild and domestic birds will be presented.

The immunosensor were developed by the successive modification of gold[1] as well as glassy carbon electrodes[2]. The whole antibody or their fragments have been applied as the sensing elements. The complex between virions and specific antibody adsorbing on a surface of an electrode forms an insulating layer. This phenomenon, which is a base of ion – channel mimetic type of immunosensors, can be monitored by the electrochemical impedance spectroscopy (EIS) in the presence of $[Fe(CN)_6]^{3-/4-}$ as a redox marker. The another type of immunosensors are based on redox active layers incorporated dipyrromethene -Cu(II)[3] complexes. The changes of electrochemical parameters of redox centres upon target analyte binging are the base of analytical signal generation.

The detection limit in the fM range has been achieved with genosensors incorporated with ssDNA decorated with Co(II)-porphyrin[4], as well as with 3-iron bis (dicarbiollide)[5]. The strategy based on dipyrromenthene Cu(II) redox active monolayer or phenanthroline – Epoxy - Fe(III) complexes have been also applied for the development genosensors destined for detection of Avian Influenza viruses[6]. To face of the need of systems for simultaneous determination of few markers of one disease coming from medical diagnosis, we have developed a novel dual DNA electrochemical sensor with “signal-off“ and “signal-on“ architecture for simultaneous detection of two different sequences of DNA derived from Avian Influenza Virus type H5N1 by means of one electrode[7]. Two sequences of ssDNA characteristic for hemagglutinin decorated with ferrocene and characteristic for neuraminidase decorated with metylene blue were immobilized covalently together on the surface of one gold electrode.

Acknowledgements
This work was supported by project: This research was supported by grant No. POIG.01.01.01-14-007/08; NCBiR No. PBS2/A7/14/2014, project 679/N – BELGIUM /2010 and COST Action CM1005.

References

1. U. Jarocka, R. Sawicka, A. Góra-Sochacka *et al. Biosens. Bioelectron.* **2014**, *55*, 301-306.
2. U. Jarocka, H. Radecka, T. Malinowski, L. Michalczuk, J. Radecki *Electroanalysis* **2013**, *25*, 433.
3. U. Jarocka, R. Sawicka, A. Stachyra *et al. Anal. Bioanal. Electrochem.* **2015**, *407*, 7807.
4. I. Grabowska, D. G. Singleton, A. Stachyra *et al. Chem.Commun*. **2014**, *50*, 4196.
5. I. Grabowska, A. Stachyra, A. Góra-Sochacka *et al. Biosens. Bioelectron.* **2014**, 51, 170.
6. K. Malecka, A. Stachyra, A. Góra-Sochacka *et al. Biosens. Bioelectron.* **2015**, 65, 427.
7. I. Grabowska, K. Malecka, A. Stachyra *et al. Anal. Chem.* **2013**, 85, 10167.

Saturday, November 4

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Frank Marken and Kamil Wojciechowski
09:00-09:40	T02	**Lars J.C. Jeuken** Supramolecular Electrode Assemblies in Bioelectrochemistry
09:40-10:00	K03	**Alain Walcarius** Electrogeneration of Mesoporous Silica Films with Vertically Ordered Nanochannels for Chemical Sensing
10:00-10:15	SC01	**Pavel Zhurauski** Self-assembled Gold Nanoparticles for Impedimetric and Amperometric Detection of a Prostate Cancer Biomarker
10:15-10:30	SC02	**Fangyuan Zhao** A Solar Nernstian Biosupercapacitor Based on Cyanobacterial Photosynthetic Complexes
10:30-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: Lars J. C. Jeuken and Hanna Radecka
11:00-11:40	T03	**Paweł Krysiński** Surface- and Core-Modified Nanoferrites as Tools for Magnetic Field-Assisted Targeted Drug Delivery
11:40-12:00	K04	**Tan-Phat Huynh** Precipitation of Inorganic Phases Through a Photoinduced pH Jump: from Vaterite Spheroids and Shells to ZnO Flakes and Hexagonal Plates
12:00-12:20	K05	**Barbara Jachimska** Self-assembling Behavior of Proteins: Effect of the Interaction between Protein and Surface
12:20-12:35	SC03	**Stanislav Trashin** Towards Point-of-Care diagnostic of Toxocariasis: Electrochemical and Photoelectrochemical Magnetosensor with Nanobodies
12:35-12:50	SC04	**Kamila Łępicka** A Multi-composite Supercapacitor with a Dual Anode and a Dual Cathode
13:00-14:30		**Group photo and Lunch**
14:30-16:20		**Afternoon session 1** Chairs: Paweł Krysiński and Tan-Phat Huynh
14:30-15:10	T04	**Alexander Kuhn** Chiral Recognition with Tailored Porous Metal Layers

15:10-15:30	K06	**Alessandra Maria Bossi** Molecularly Imprinted Nanomaterials Targeting Linear and Structured Peptides
15:30-15:50	K07	**Andrew James Gross** Buckypaper Bioelectrodes: Emerging Materials for Implantable and Wearable Bioelectronics Devices
15:50-16:10	K08	**Gerd-Uwe Flechsig** Structure of DNA Layers on Gold Surfaces Studied by Millisecond-resolved EQCM and H/D Kinetic Isotope Effects
16:10-16:25	SC05	**Felipe Conzuelo** Evaluation of (Bio)photocatalysts for Energy Conversion by Means of Scanning Photoelectrochemical Microscopy

16:25-17:00 **Coffee break**

17:00-18:50 **Afternoon session 2**
Chairs: Alessandra M. Bossi and Trashin Stanislav

17:00-17:40	T05	**Jacek Lipkowski** Application of IR Spectroscopy to Study Thin Films of Biomolecules at the Electrified Metal-Solution Interface
17:40-18:00	K09	**Fred Lisdat** Cytochrome *c* as Valuable Building Block in Multilayered Architectures of Biocatalysts on Electrodes
18:00-18:20	K10	**Wolfgang Kaiser** Surface-immobilized Electrically Actuated DNA Layers for the Measurement of Binding Kinetics, Stokes Radius and Conformational Changes of Proteins
18:20-18:35	SC06	**Adam Kolodziej** Electrochemical Stability of Thiols and Disulfides Assembled on Gold in Physiological Medium
18:35-18:50	SC07	**Laurent Bouffier** Straightforward Control of Chemical Surface Gradients by Wireless Electrochemistry

19:00-20:00 **Dinner**

20:00-22:00 **Poster session**

T02. Supramolecular Electrode Assemblies in Bioelectrochemistry

Theodoros Laftosglou, Ee-Taek Hwang, George Heath,
Valentin Radu, Mengqiu Li, Lars J. C. Jeuken

School of Biomedical Sciences, University of Leeds, Leeds, LS2 9JT, United Kingdom
L.J.C.Jeuken@leeds.ac.uk

For more than three decades, the field of bioelectrochemistry has provided novel insights into the catalytic mechanisms of enzymes, the principles that govern biological electron transfer, and has elucidated the basic principles for bioelectrocatalytic systems. Progress in biochemistry, bionanotechnology, and our ever increasing ability to control the chemistry and structure of electrode surfaces has enabled the study of ever more complex systems with bioelectrochemistry. In this tutorial lecture, I will highlights developments over the last one to two decades, where supramolecular approaches have been employed to develop electrode assemblies that increase enzyme loading on the electrode or create more biocompatible environments.

Supramolecular chemistry is concerned with systems that are comprised of molecular units that are assembled by weak interactions; they are primarily focused on electrostatic, van der Waals and hydrophobic interactions, and, more recently, metal coordination chemistry. Several approaches are highlighted in this lecture: (1) Supramolecular approaches to accommodate integral membrane enzymes; (2) The use of nano- and meso-porous electrodes or co-assemble of nanoparticles to enhance electroactive surface areas of electrodes; and (3) the use of layer-by-layer assembly.

Many redox enzymes are oxidoreductases and an important group of them reside in bacterial, mitochondrial or chloroplast (inner) membranes. Although many approaches have been developed to study and utilize redox proteins and enzymes in bioelectrochemistry, significantly less strategies have been developed for membrane proteins compared to globular proteins. Here, I will provide a brief overview of the strategies used to make electrodes suitable for membrane proteins.

The electrochemical surface area of electrodes can be greatly enhanced if either the electrode is structured or modified with length scales comparable to that of the redox proteins. Several key examples will be covered in this tutorial lecture, including mesostructured electrodes (although these are not strictly supramolecular approaches) and electrodes modified with carbon nanotubes and gold nanoparticles.

Finally, Layer-by-Layer (LbL) deposition has the ability to either increase enzyme loading on the electrode or to create well organized layers consisting of different enzymes that work in tandem in multistep reactions. For bioelectrochemical applications, the LbL systems either have to be permeable to electron mediators, which can be proteins, or the LbL system has to be conductive.

References

1. L.J.C. Jeuken, Structure and Modification of Electrode Materials for Protein Electrochemistry In: Jeuken, L.J.C. (ed.) Biophotoelectrochemistry: From Bioelectrochemistry to Photosynthesis, Berlin: Spinger, **2016**, Chapter 2, pp 43-73.
2. T. Laftsoglou, L. J. C. Jeuken *Chem. Commum*. **2017**, *53*, 3801.
3. L. J. C. Jeuken *Nat. Prod. Rep.* **2009**, *26*, 1234.

K03. Electrogeneration of Mesoporous Silica Films with Vertically Ordered Nanochannels for Chemical Sensing

Alain Walcarius

Laboratoire de Chimie Physique et Microbiologie pour l'Environnement,
Unité Mixte de Recherche UMR 7564, CNRS – Université de Lorraine
405, rue de Vandoeuvre, F-54600 Villers-les-Nancy, France
alain.walcarius@univ-lorraine.fr

Nanostructuration of electrode surfaces has emerged as a powerful mean to improve the performance of electrochemical devices by providing high molecular accessibility and rapid mass transport via diffusion, and increasing the electroactive surface areas in comparison to the geometric ones, and/or designing confined platforms to host suitable reagents.[1] This lecture will highlight how the soft template technology can be associated to sol-gel electro-generation for preparing new types of mesoporous electrodes, exhibiting unique vertical pore orientation and bearing organo-functional groups, for possible applications in electroanalysis. Ordered mesoporous films with mesochannels oriented perpendicular to the solid surface can be generated by electro-assisted self-assembly (EASA).[2] The method combines the electrochemically-driven self-assembly of surfactants onto an electrode surface and sol-gel electro-assisted deposition by electrochemical pH tuning at the electrode/solution interface to induce condensation of the precursors in a controlled way.[3] Such vertical orientation of small pores (2-3 nm in diameter) induces fast mass transport rates, which can be exploited for electroanalytical purposes.[4] These films also exhibit permselective properties based on charge[5] and size selectivity,[6] with potential applications in molecular sieving[6] or anti-(bio)fouling surfaces.[7] The possibility to generate organically-functionalized oriented mesoporous thin films will be also discussed, showing notably the influence of the organic group type and content on the level of mesostructural order; their application as electrochemical sensors will be exemplified for the detection of metal ions subsequent to preconcentration.[8] Finally, the electrochemically-assisted generation of highly ordered azide-functionalized mesoporous silica will be exploited as a versatile platform towards hybrid films with perpendicular mesochannels via 'Click Chemistry'.[9] When these films are functionalized with redox-active moieties, they enable charge transport reactions to occur in such isolating media, via a mechanism of electron hopping between adjacent sites,[10] and this can be exploited for long-range charge transport, e.g., to mediate the electrochemical transformation of size-excluded redox probes,[6] or for the indirect amperometric detection of non-electroactive species.[11]

References

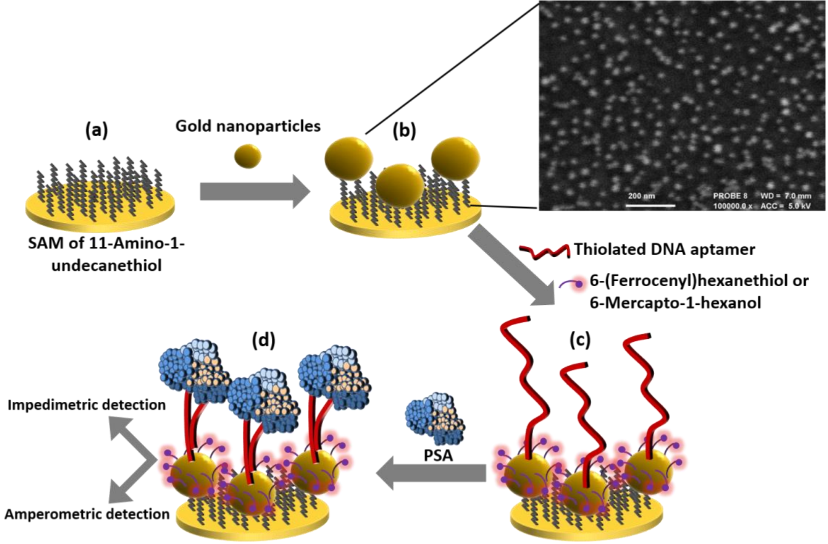
1. A. Walcarius *Chem. Soc. Rev*. **2013**, *42*, 4098.
2. A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja *Nature Mater*. **2007**, *6*, 602.
3. A. Goux, M. Etienne, E. Aubert *et al*. *Chem. Mater*. **2009**, *21*, 731.
4. F. Yan, X. Lin, B. Su *Analyst* **2016**, *141*, 3482.
5. C. Karman, N. Vilà, A. Walcarius *ChemElectroChem* **2016**, *3*, 2130.
6. N. Vilà, E. André, R. Ciganda, J. Ruiz, D. Astruc, A. Walcarius *Chem. Mater*. **2016**, *28*, 2511.
7. M. B. Serrano, C. Despas, G. Herzog, A. Walcarius *Electrochem. Commun*. **2015**, *52*, 34.
8. G. Herzog, E. Sibottier, M. Etienne, A. Walcarius *Faraday Discuss.* **2013**, *164*, 259.
9. N. Vilà, J. Ghanbaja, E. Aubert, A. Walcarius *Angew. Chem. Int. Ed.* **2014**, *53*, 2945.
10. N. Vilà, A. Walcarius *Electrochim. Acta* **2015**, *179*, 304.
11. C. Karman, N. Vilà, C. Despas, A. Walcarius *Electrochim. Acta* **2017**, *228*, 659.

SC01. Self-assembled Gold Nanoparticles for Impedimetric and Amperometric Detection of a Prostate Cancer Biomarker

Pavel PZ. Zhurauski,[a] Pawan PJ. Jolly,[a] Jules L. JLH. Hammond,[a] Anna AM. Miodek,[a]
Susana SL. Liébana,[b] Tomas TB. Bertok,[c] Jan JT. Tkáč,[c] Pedro PE. Estrela,[a]

[a] Department of Electronic and Electrical Engineering, University of Bath, Bath BA2 7AY, UK
[b] Applied Enzyme Technology Ltd., Gwent Group Ltd., Pontypool NP4 0HZ, UK
[c] Department of Glycobiotechnology, Institute of Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, 845 38 Bratislava, Slovak Republic
pavelzhurauski@zimmerpeacock.com

A label-free dual-mode impedimetric and amperometric aptasensor platform was developed using a simple surface chemistry step to attach gold nanoparticles (AuNPs) to a gold planar surface. As a case study, the strategy was employed to detect prostate specific antigen (PSA), a biomarker for prostate cancer. An anti-PSA DNA aptamer was co-immobilized with either 6-mercapto-1-hexanol (MCH) or 6-(ferrocenyl)hexanethiol (FcSH) for both impedimetric or amperometric detection, respectively. We show that the use of AuNPs enables a significant improvement in the limit of impedimetric detection as com- pared to a standard binary self-assembled monolayer aptasensor. A PSA detection of as low as 10 pg/mL was achieved with a dynamic range from 10 pg/mL to 10 ng/mL, well within the clinically relevant values, whilst retaining high specificity of analysis. The reported approach can be easily generalized to various other bioreceptors and redox markers in order to perform multiplexing.



Scheme of the AuNP-modified aptasensor showing how either impedimetric or amperometric detection can be used depending on whether the DNA aptamer is co-immobilised with MCH or FcSH

SC02. A Solar Nernstian Biosupercapacitor Based on Cyanobacterial Photosynthetic Complexes

F. Zhao,[a] F. Conzuelo,[a] A. Ruff,[a] T. Bobrowski,[a] Volker Hartmann,[b]
M.M. Nowaczyk,[b] M. Rögner,[b] W. Schuhmann[a]

[a] *Analytical Chemistry – Center for Electrochemical Sciences,*
Ruhr-Universität Bochum, Bochum, Germany
[b] *Plant Biochemistry, Ruhr-Universität Bochum, Bochum, Germany*
fangyuan.zhao@rub.de

With the aim of looking for alternative energy sources others than traditional fossil fuels, electrical energy biodevices utilizing enzymes as electrocatalysts have been increasingly explored due to their environmental sustainability as well as their high activities and catalytic efficiencies. In addition to biofuel cells, which directly convert chemical energy into electric energy, a novel bioelectronic device, i.e., a self-charging biosupercapacitor, has recently emerged. This hybrid biodevice does not only convert chemical energy stored in the form of a fuel into electric energy but also is capable to store the generated electric power[1]. In nature, photosystem 2 (PS2) and photosystem 1 (PS1) work in series to drive oxygenic photosynthesis. Inspired by the unique light-harvesting properties and strikingly large quantum efficiencies of these protein complexes, we have previously fabricated individual photoelectrodes by coupling of photosynthetic proteins isolated from the cyanobacterium *T. elongatus* to electrode surfaces using an Os-complex-modified redox polymer as wiring matrix[2,3]. In this work, we present a solar Nernstian biosupercapacitor assembled by coupling of a PS1-based photocathode and a PS2-based photoanode. As we have shown before[4], the Os-complex-modified redox polymer revealing identical potentials for both bioelectrodes can be used for the design of a self-charging biosupercapacitor. Upon the absorption of visible light, PS2 is capable of extracting electrons from water used as a fuel, while PS1 acts as a charge pump providing high-energy electrons after light-induced charge separation. These reactions provide the driving force for the reduction and oxidation of a specifically designed redox polymer at the anode and cathode, respectively, making the charging of the biodevice under irradiation possible. The fabricated solar biodevice shows potential in acting as a self-charging and thus self-powered biodevice, which is of particular interest for the future design of sensing systems.

Acknowledgements

The authors are grateful to the European Commission in the framework of the ITN “Bioenergy” (PITN-GA-2013-607793), the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft, and the DIP project “Nanoengineered Optobioelectronics with Biomaterials and Bioinspired Assemblies” funded by the DFG for financial support. F.Z. is grateful for the support by CSC.

References

1. D. Pankratov, Z. Blum, S. Shleev *ChemElectroChem*, **2014**, *1*, 1798.
2. A. Badura, D. Guschin, B. Esper, T. Kothe, S. Neugebauer, W. Schuhmann and M. Rögner *Electroanal.* **2008**, *20*, 1043.
3. A. Badura, D. Guschin, T. Kothe, M. J. Kopczak, W. Schuhmann, M. Rögner *Energy Environ. Sci.* **2011**, *4*, 2435.
4. D. Pankratov, F. Conzuelo, P. Pinyou, S. Alsaoub, W. Schuhmann, S. Shleev *Angew. Chem. Int. Ed.*, **2016**, *55*, 15434.

T03.

Surface- and Core-Modified Nanoferrites as Tools for Magnetic Field-Assisted Targeted Drug Delivery

Aleksandra Rękorajska,[a] Dorota Nieciecka,[a] Anna Nieścioruk,[a] Anna Puszko,
Aleksandra Misicka,[a] Gary J. Blanchard,[b] Paweł Krysiński[a]

[a] *Faculty of Chemistry, University of Warsaw, 02-093 Warsaw, Poland*
[b] *Department of Chemistry, Michigan State University, E. Lansing, MI 48824, USA*
pakrys@chem.uw.edu.pl

Superparamagnetic nanoparticles (SPNs) have attracted wide attention due to their unique magnetic properties, high surface area-to-volume ratio, and the ability to control their core and surface chemistry. The superparamagnetic behavior makes SPNs ideal candidates as carrier platforms in magnetically-driven targeted drug delivery and hyperthermia. In such a therapeutic approach, the drug/SPN carrier conjugate can be guided to the specific site with an aid of magnetic field, release the drug payload or/and become localized sources of heat, leading to the cell death. If the SPN core is labelled with "soft" β^- emitting radionuclide (e.g., ^{161}Tb), it will allow for simultaneous direct irradiation of tumor, solely from within its tissue. This combined, multimodal approach is particularly promising in the treatment of tumors resistant to classical therapies.

We present here three examples of applications of SPNs: i) hydrophilic nanoparticles conjugated covalently with biologically active molecule - a "vector" peptide targeting specific tumors, ii) hydrophobic SPNs confined only within the bilayer lipid membranes of liposomes and cubosomes, iii) Tb-doped SPNs – initial studies of their behavior from the point of view of synergic effect of radiotherapy and hyperthermia.

Acknowledgements

Funds were provided by NSC grant OPUS 11 UMO-2016/21/B/ST4.02133.

References

1. A. Joniec, S. Sek, P. Krysinski *Chem. – Eur. J.* **2016**, *22*, 17715.
2. A. Niescioruk, D. Nieciecka, A. K. Puszko *J. Nanopart. Res.*, **2017,** 19:160.

K04. Precipitation of Inorganic Phases Through a Photoinduced pH Jump: from Vaterite Spheroids and Shells to ZnO Flakes and Hexagonal Plates

Tan-Phat Huynh,[a,b] Carsten Pedersen,[a] Nina Kølln Wittig,[a] and Henrik Birkedal[a]

[a] *Department of Chemistry & iNANO, Aarhus University,*
14 Gustav Wieds Vej, 8000 Aarhus, Denmark
[b] *Laboratory of Physical Chemistry, Faculty of Science and Engineering, Åbo Akademi University,*
Porthaninkatu 3-5, 20500 Turku, Finland
tan.huynh@abo.fi

A new way to precipitate inorganic phases through pH jumps was driven by optical excitation of a photobase. The level of the pH jumps is manipulated by either the wavelength range or illumination time used. The method is demonstrated by precipitation of $CaCO_3$ and ZnO from their supersaturated precursors precipitation. Vaterite spheres and shells for $CaCO_3$ and flakes and hexagonal plates for ZnO are formed under various controllable conditions. Notably, ZnO films could be formed and patterned directly on quartz substrates using a photomask. The film thickness was easily controlled by illumination time. This method is an important step towards self-organized crystallization with spatio-temporal control fully in the hands of the experimenter.

References

1. H. Birkedal, In New Perspectives on Mineral Nucleation and Growth: From Solution Precursors to Solid Materials (Eds.: A. E. S. Van Driessche, M. Kellermeier, L. G. Benning, D. Gebauer), Springer International Publishing: Cham, **2017**, 199-210.
2. M. Irie, *J. Am. Chem. Soc*. **1983**, *105*, 2079.

K05. Self-assembling Behavior of Proteins: Effect of the Interaction between Protein and Surface

Barbara Jachimska

J. Haber Institute of Catalysis and Surface Chemistry, PAS,
Niezapominajek 8, 30-239 Cracow, Poland
ncjachim@cyf-kr.edu.pl

An important factor determining the use of biomaterials is their interactions with systemic fluids. These interactions determine, among others, biocompatibility of a given material. This is why the issue of protein adsorption on solid surfaces is very topical and important.

The properties of the adsorbed protein layer are highly dependent on the shape, effective charge and structure of the protein as these factors influence surface affinity, protein surface coverage and hydration of the layer. In addition, the polarity, hydrophobicity and surface roughness affect the reversibility of the protein adsorption process. Preferred binding orientation has been confirmed as a results of the protein surface interactions induced by the heterogeneous surface of protein molecules, which can further affect protein conformational transitions, orientation or deformation.

Analysis of the experimental data shows that there are still inconsistent opinions about the mechanism of protein adsorption concerning adsorption kinetics, structural reorientation or conformation and protein aggregation whether in a solution or on the surface. As protein adsorption depends on several factors, which many are irreversible processes consequently producing various final effects for the same protein. Therefore, the development of new research techniques makes it possible to study adsorption with increasing accuracy: from measurements of adsorption kinetics at high protein concentrations to detecting even a single protein molecule adsorbed on a surface. It is also possible to trace changes in the orientation and structural properties of proteins in the adsorbed state. Development of theoretical methods makes it possible to determine the interaction of protein molecules with a surface and to visualize the whole process at the atomic level that is not available experimentally. Simulations can show not only how proteins adsorb to the surfaces, but also provide understanding of what the driving forces are and how they can be controlled through surface chemistry. A combination of experimental studies with theoretical calculations should enable continued progress in understanding of the behavior of proteins on solid surfaces and how bioactivity can be preserved by retaining the protein secondary and tertiary structures.

The mechanisms of interaction of functional materials with different types of proteins present in the plasma, together with the analysis of conformational changes and reorganization of protein structures on the functional surfaces has great cognitive value. It will also contribute to a better understanding of the physicochemical mechanisms of creating protein layers with controlled architecture and functionality.

Acknowledgements
This work was supported by Grant NCN OPUS 2016/23/B/ST5/02788.

SC03. Towards Point-of-care diagnostic of Toxocariasis: Electrochemical and Photoelectrochemical Magnetosensor with Nanobodies

Stanislav Trashin,[a] Francisco Morales-Yanez,[b,c] Katja Polman,[c]
Serge Muyldermans,[b] Karolien De Wael[a]

[a]AXES Research Group, Department of Chemistry,
University of Antwerp, Antwerp, Belgium,
[b]Laboratory of Cellular and Molecular Immunology,
Vrije Universiteit Brussel, Brussels, Belgium
[c] Department of Biomedical Sciences, Unit of Medical Helminthology,
Institute of Tropical Medicine, Antwerp, Belgium
stanislav.trashin@uantwerpen.be

Human toxocariasis is the most cosmopolitan zoonotic helminthiasis worldwide. The occurrence of the disease ranges from 2-5% in Western countries to 93% in tropical areas. In severe cases, the parasite can affect the liver, lungs, nervous system, heart, and eyes. Children are at the highest risk because they play outside and may ingest parasite's eggs by accident. The symptoms of toxocariasis are not specific and, thus, an immunological test must be conducted to discover the infection. Modern diagnostic immunological tests aim to detect the specific *Toxocara canis* excretory-secretory (TES) antigen. Detection of TES antigen circulating in blood is non-trivial because of its low concentration and unsatisfying sensitivity and specificity of the traditional ELISA method. Moreover, the occurrence of the disease is the highest in rural areas and countries with poor socio-economic conditions. Thus, an efficient yet low-cost point-of-care diagnostic tool is necessary to tackle the spread of toxocariasis and reduce the rate of complications. Recently, we obtained TES specific nanobodies (single domain bioengineering camel antibody's fragments[1]) that showed good diagnostic performance in ELISA essays, but the sensitivity was still unsatisfying. The problem was solved by using magnetic beads coated by bivalent nanobodies as biorecognition element, and an amperometric detector as a signal transducer. This format opened opportunities for development a low-cost point-of-care test. The biocatalytic-electrochemical redox cycling of tetramethylbenzidine led to a fast and sensitive response. The electrochemical essay showed advantageous analytical performance with a limit of detection (LOD) of 3 pg/ml in phosphate buffer. It was more than 10 times better than the LOD for an optimized ELISA with the same immunoreagents. Excellent diagnostic performance of the electrochemical assay was demonstrated on human serum spiked-in with TES. The developed immunoassay has been combined with the photoelectrochemical detection principle that we recently formulated.[2] The detection relies on photocatalytic oxidation of a redox reporter followed by its consequent reduction at the electrode.[2,3] This brings several advantages, such as instance baseline correction and replacement of hydrogen peroxide by air oxygen. Superiority and limitations of this approach are discussed. The elaborated essay needs only standard ELISA kit reagents, yet it works faster and does not require access to a laboratory. This essay is the first prototype for an affordable point-of-care device for sensitive and specific toxocariasis diagnostic.

References

1. S. Muyldermans *Annu. Rev. Biochem*. **2013**, *82*, 775.
2. S. Trashin,V. Rahemi, K. Ramji, L. Neven, S. M. Gorun, K. De Wael *Nat. Commun.* **2017**, *8*, 16108.
3. A. Alvares-Martin, S. Trashin, M. Cuykx, A. Covaci, K. De Wael, K. Janssens *Dyes Pigm.* **2017**, *145*, 376.

SC04. A Multi-composite Supercapacitor with a Dual Anode and a Dual Cathode

Kamila Łępicka,[a] Piotr Pieta,[a] Ruma Gupta,[b] and Wlodzimierz Kutner[c]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences,*
Kasprzaka 44/52, 01-224 Warsaw, Poland
[b] *Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India 400085*
[c] *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

A redox conducting polymer film was prepared by electropolymerization of a *meso*-*N*,*N*'-bis-(salicylidene)-2,3-butanediaminonickel(II)] monomer, *meso*-Ni(II)-SaldMe.[1] Then, electrochemical and capacitive properties of poly[*meso*-Ni(II)-SaldMe] were characterized by cyclic voltammetry, piezoelectric microgravimetry, electrochemical impedance spectroscopy, and galvanostatic charging-discharging. The polymer film revealed electroactivity in the potential range of 0.30 to 1.10 V vs. Ag/Ag^+ and high durability. Specific capacitance, *SC*, of the film was ~210 F g^{-1} at the scan rate of 5 mV s^{-1}. Next, the poly(*meso*-Ni(II)-SaldMe) film was utilized to fabricate a new laboratory model of an asymmetric supercapacitor with a dual anode and a dual cathode. Polypyrrole (PPy) and poly[*meso*-Ni(II)-SaldMe] were separately deposited on a carbon paper electrode preliminary coated with a film of reduced graphene oxide, RGO, and then used as a positive electrode (dual anode). The negative electrode (dual cathode) was prepared by deposition of a C_{60}-based polymer and PPy on the (carbon paper)/RGO electrode. The fabricated device was operated in the voltage range of 0 to 2.20 V in the 0.1 M $(TBA)PF_6$ solution of propylene carbonate, thus allowing for maximum charging of all composite electrodes and delivering a high energy density of 102.60 W h kg^{-1} at the power density of 12.21 kW kg^{-1}. The life-time of charge-discharge cycling of this supercapacitor was excellent retaining 91% of its *SC* after 10 000 consecutive cycles.

References

1. K. Łępicka, P. Pieta, A. Shkurenko, P.Borowicz, M. Majewska, M. Rosenkranz, S. Avdoshenko, A. A. Popov, W. Kutner *J. Phys. Chem. C* **2017,** *121*, 16710.

T04. Chiral Recognition with Tailored Porous Metal Layers

Alexander Kuhn,[a] Thittaya Yutthalekha,[a,b,c] Sunpet Assavapanumat,[a,c] Chularat Wattanakit,[c]
Veronique Lapeyre,[a] Somkiat Nokbin,[b] Chompunuch Warakulwit,[b] Jumras Limtrakul[c]

[a] *Univ. de Bordeaux, CNRS, ISM, UMR 5255, 16 Avenue Pey Berland, FR-33607 Pessac, France*
[b] *Department of Chemistry and NANOTEC Center for Nanoscale Materials Design*
for Green Nanotechnology, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand
[c] *School of Energy Science and Engineering, School of Molecular Science and Engineering,*
Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand
kuhn@enscbp.fr

Artificial chiral recognition is a major challenge, due to various potential applications ranging from sensing to catalysis and separation science. In this context, molecular imprinting is a well-known approach for generating materials with enantioselective properties, and it has been successfully employed using polymers.[1] However, it is particularly difficult to synthesize chiral metal matrices by this method. We present here the elaboration of chiral imprinted mesoporous metal, obtained by the electrochemical reduction of platinum salts in the presence of a liquid crystal phase[2] and chiral template molecules.[3] The porous platinum retains its chiral character after removal of the template molecules and exhibits a large active surface area due to its mesoporosity. Most importantly, it shows a very significant discrimination between two enantiomers when they are studied using these materials as electrodes in Differential Pulse Voltammetry (see Figure 1).[4] We also could demonstrate that such nanostructured metals are able to break the symmetry during the electrochemical conversion of prochiral molecules[5] and optimizing the experimental parameters allows achieving over 90% enantiomeric excess.[6] Therefore these designer surfaces open new promising horizons not only for electroanalysis, but also for efficient enantioselective electrosynthesis.

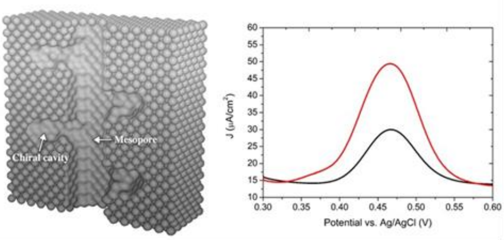


Figure 1. Metal structure after template removal, composed of chiral cavities and mesoporous channels (left). Differential pulse voltammograms in 4 mM D-DOPA (small peak) and L-DOPA (high peak) recorded with a chiral mesoporous platinum electrode imprinted with R-mandelic acid (right).[3,4]

References

1. K. Haupt, A. Linares, M. Bompart, B. Bui, in Molecular Imprinting, Vol. 325 (Ed.: K. Haupt), Springer: Berlin Heidelberg, **2012**, pp. 1-28.
2. G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang *Science* **1997**, *278*, 838.
3. C. Wattanakit, Y. Bon Saint Côme, V. Lapeyre, P. A. Bopp, M. Heim, S. Yadnum, S. Nokbin, C. Warakulwit, J. Limtrakul, A. Kuhn *Nat. Comm.* **2014**, 5:3325
4. T. Yutthalekha, C. Warakulwit, J. Limtrakul, A. Kuhn *Electroanalysis* **2015,** *27*, 2209.
5. T. Yutthalekha, V. Lapeyre, S. Nokbin, C. Warakulwit, J. Limtrakul, A. Kuhn *Nat. Comm.* **2016**, 7:12678.
6. C. Wattanakit, T. Yutthalekha, S. Assavapanumat, V. Lapeyre, J. Limtrakul, A. Kuhn, **2017**, *submitted*.

K06.

Molecularly Imprinted Nanomaterials Targeting Linear and Structured Peptides

Alessandra Maria Bossi

Biotechnology Dept., University of Verona, Verona, Italy
alessandramaria.bossi@univr.it

Molecularly imprinted polymers (MIPs) are tailor-made biomimetic materials prepared by template assisted synthesis: the monomers and the crosslinker are polymerized in the presence of the target analyte, called the template, so that stereo-chemical template-complementary prints are left on the growing polymer. MIPs exhibit exceptional recognition properties for the template, possessing selectivity, specificity and affinity on the par of natural antibodies[1-3], but being made of plastic, MIPs are resistant to thermal stress and to extreme pHs, cheaper in production respect to the biological macromolecules and suitable to mass fabrication.

With the aim to improve the determination of biomarkers in clinical sensing platforms, we explored the rational design and the preparation of MIP nanoparticles (nanoMIPs) suitable for the recognition of peptide epitopes, both when these were unstructured random coil peptides and when these are structured, so to mimic the structural constrains of peptides contained in native folded proteins.

NanoMIPs addressed at the recognition of linear and structured peptides were synthesized by radical polymerization of acrylamido-based monomers. The prepared materials were characterized physico-chemically and a Z-average of ~60 nm was observed. The nanoMIP compositions were confirmed by XPS analysis. The binding isotherms demonstrated nanomolar affinities for the templates and ability to discriminate peptide structures.[4] The mean number of binding sites per nanoparticle was estimated. When used as plastic antibodies in pseudoELISAs or as a recognition element hyphenated to MALDI-TOF MS, the nanoMIPs demonstrated the ability to recognize the target peptide in serum samples.

The results demonstrated the possibility to prepare tailor made nanoMIPs both for linear and for structured peptides, letting foresee a new class of pluri-dimensional MIP receptors, sensitive to protein structural modifications, that would contribute in the determination of local protein structural changes connected to the insurgence of pathological states.

References

1. C. Alexander, H. S. Andersson, L. I. Ande *et al. J. Mol. Recognit.*, **2003**, *19*, 106.
2. A. Bossi, F. Bonini, A. P. Turner, S. A. Piletsky *Biosens. Bioelectronics*, **2007**, *22*, 1131.
3. Y. Hoshino, T. Kodama, Y. Okahata, KJ. Shea *J. Am. Chem. Soc.* **2008**, *130*, 15242.
4. L. Cenci, G. Guella, E. Andreetto, E. Ambrosi, A. Anesi, A. M. Bossi *Nanoscale*, **2016**, *8*, 15665.

K07.

Buckypaper Bioelectrodes: Emerging Materials for Implantable and Wearable Bioelectronics Devices

Andrew J. Gross, Xiaohong Chen, Fabien Giroud, Michael Holzinger, Serge Cosnier

Department of Molecular Chemistry, Université Grenoble Alpes, 38000 Grenoble, France
andrew.gross@univ-grenoble-alpes.fr

Buckypaper is an attractively assembled macroscopic form of carbon nanotubes resembling a self-supporting electronic paper with great potential for future bioelectronics devices from artificial muscles to self-powered health and environmental sensors[1-4]. This talk will summarize recent developments and advances in buckypaper in the context of enzymatic biofuel cells and biosensors. Our recent work on the fabrication, characterization and catalysis of multi-walled carbon nanotube buckypapers prepared with embedded 'precision' polymers, redox molecules and enzymes will be discussed[3-5]. Fresh results on the fabrication and testing of paper-based buckypaper supercapacitors will also be presented.

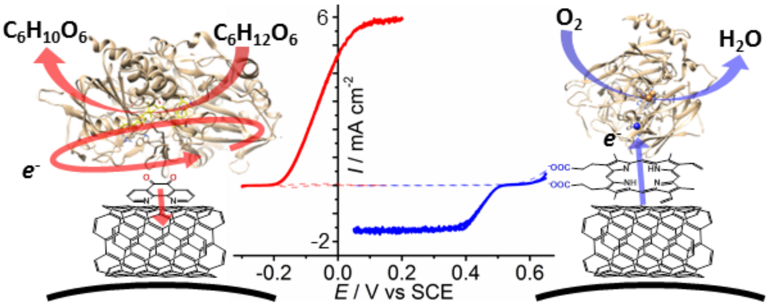


Figure 1. Catalytically-powerful buckypaper bioelectrodes with embedded redox molecules[6]

References

1. S. Cosnier, A. J. Gross, A. L. Goff, M. Holzinger *J. Power Sources* **2016**, 325, 252.
2. E. Katz, in Implantable Bioelectronics: Devices, Materials and Applications. Wiley-VCH, **2014**.
3. F. Giroud, A. J. Gross, D. Junior Faggion, M. Holzinger, C. E. Maduro de Campos, J. J. S. Acuna, J. B. Domingos, S. Cosnier *Electrochem. Soc.* **2017**, *164*, H3052.
4. A. J. Bandodkar, I. Jeerapan, J. Wang *ACS Sens.* **2016**, 1, 464.
5. A. J. Gross, M. P. Robin, Y. Nedellec, R. K. O'Reilly, D. Shan, S. Cosnier *Carbon* **2016**, *107*, 542.
6. A. J. Gross, X. Chen, F. Giroud, C. Abreu, A. Le Goff, M. Holzinger, S. Cosnier *ACS Catal.*, **2017**, *7*, 4408.

K08. Structure of DNA Layers on Gold Surfaces Studied by Millisecond-resolved EQCM and H/D Kinetic Isotope Effects

Sarasi K.K. Galagedera, Jörg Peter, Gerd-Uwe Flechsig

University at Albany, SUNY, Dept. of Chemistry, Albany, NY 12222, United States
gflechsig@albany.edu

We have investigated the interaction of hexammine ruthenium(III) (RuHex) and hexammine cobalt(III) (CoHex) with DNA on gold electrodes by electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry. These complexes interact with DNA both electrostatically and by formation of hydrogen bonds. We have observed a large frequency change of ca. 25 Hz (Fig. 1) upon 450 mV potential jumps that could not be explained by a loss or gain of complex cations or counter anions. The EQCM response with high density DNA layers occurred only when a proper potential jump around the redox potential of RuHex or CoHex was applied. For CoHex, it took 30 seconds to reach a new stable frequency in contrast to only 240 ms in case of RuHex. Without RuHex and CoHex, a very small frequency response (4 Hz) occurred within 80 ms. Viscoelasticity of the DNA-SAM may be influenced by the interaction with the different complex ions. CoHex is known to influence the secondary and tertiary structure of DNA forming intermolecular bridges between strands.[1] This mechanism was supported by the observed major H/D kinetic isotope effects with CoHex that we found for voltammetry and EQCM studies in deuterium oxide-based electrolytes. With RuHex, this H/D-effect was significantly smaller. DNA surface coverage has great influence upon the frequency shift. We used the method of Murphy *et al*. (MCH immobilization first, DNA second)[2] to create very low density DNA layers that show a different behavior. Both redox switching of EQCM response and H/D kinetic isotope effects can shed light on the complicated structure of gold-thiol-based layers consisting of DNA and backfill molecules such as mercaptohexanol.

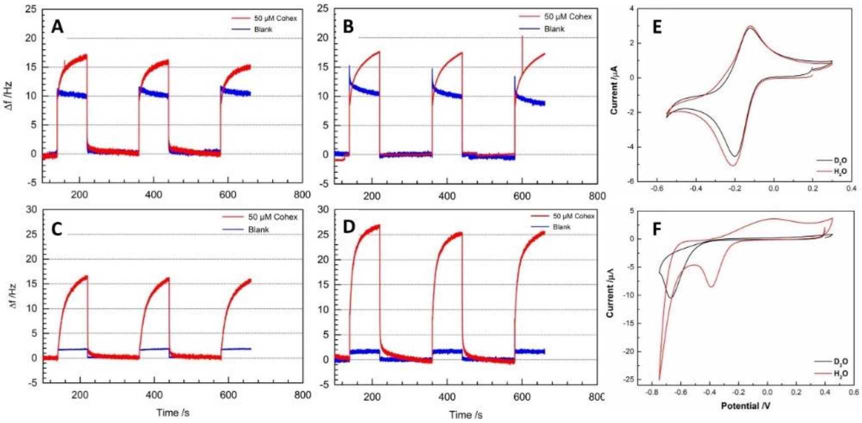


Fig. 1. EQCM response obtained with potential pulses applied to A, B) low density and C, D) high density DNA layers on gold electrodes in 10 mM TRIS buffer, pH 7.5 with A, C) D_2O and B, D) H_2O as a solvent. Voltammograms in panels E and F illustrate the kinetic isotope effect observed with high density DNA layers and 10 mM TRIS buffer containing 50 µM of E) RuHex and F) CoHex.

References

1. S. Thiyagarajan, S. S. Rajan, N. Gautham *Nucleic Acids Res.* **2004**, *32*, 5945.
2. J. N. Murphy, A. K. Cheng, H. Z. Yu, D. Bizzotto *J. Am. Chem. Soc.* **2009**, *131*, 4042.

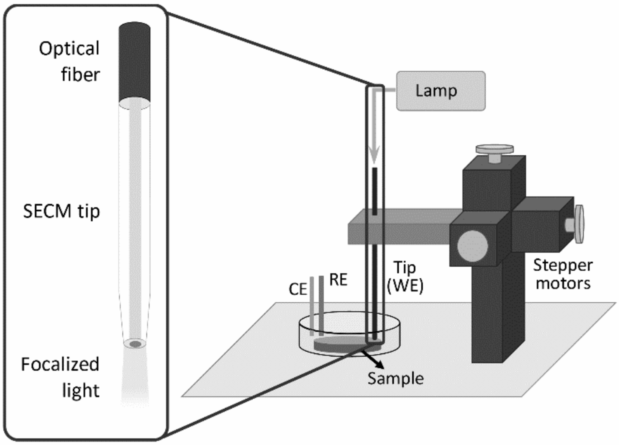
SC05. Evaluation of (Bio)photocatalysts for Energy Conversion by Means of Scanning Photoelectrochemical Microscopy

F. Conzuelo,[a] F. Zhao,[a] K. Sliozberg,[a] R. Gutkowski,[a] A. Ruff,[a] V. Hartmann,[b]
M.M. Nowaczyk,[b] M. Rögner,[b] M. Nebel,[c] N. Plumeré,[d] W. Schuhmann[a]

[a] *Analytical Chemistry – Center for Electrochemical Sciences,*
Ruhr-Universität Bochum, Bochum, Germany
[b] *Plant Biochemistry, Ruhr-Universität Bochum, Bochum, Germany*
[c] *Sensolytics GmbH, Bochum, Germany*
[d] *Center for Electrochemical Sciences – Molecular Nanostructures;*
Ruhr-Universität Bochum, Bochum, Germany
felipe.conzuelo@rub.de

A large number of photoelectrocatalytic materials based on ternary and quaternary metal oxides have been developed for their potential use as photoelectrodes for solar water splitting. Despite exhibiting promising properties, these photoelectrodes need yet to be improved concerning their limitations by poor charge separation and slow water oxidation kinetics. On the other hand, the remarkable abundance and high quantum efficiency of biological photosystems make them particularly interesting for the fabrication of biophotovoltaic devices. An extensive evaluation of both inorganic and biological systems is desired for the development of state-of-the-art devices aiming for a highly efficient performance in solar-to-chemical energy conversion.

Scanning electrochemical microscopy (SECM) is a powerful tool for the assessment of diverse materials, in which an accurately positioned microelectrode is used as a probe for the analysis of the electrochemical properties of the sample surface. As shown recently, by coupling a light fiber to the top glass-sheath of the microelectrode, local illumination of the analyzed area below the tip becomes possible. This allows to monitor local photoelectrocatalytic reactions with the SECM tip simultaneously acting as the electrochemical probe in a sample generator/tip collector arrangement (see Figure).[1,2] We present the application of this technique as a versatile tool for the local evaluation of photoelectrochemical processes at the micro scale. Examples including the analysis of semiconductor materials as well as biological photosystems integrated in suitably designed redox polymers will be shown.



Acknowledgements

The authors are grateful to the European Commission in the framework of the ITN “Bioenergy” (PITN-GA-2013-607793), the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft, and the DIP project “Nanoengineered Optobioelectronics with Biomaterials and Bioinspired Assemblies” funded by the DFG for financial support.

References

1. F. Conzuelo, K. Sliozberg, R. Gutkowski, S. Grützke, M. Nebel and W. Schuhmann *Anal. Chem.* **2017**, *89*, 1222-1228.
2. F. Zhao, N. Plumeré, M.M. Nowaczyk, A. Ruff, W. Schuhmann and F. Conzuelo *Small* **2017**, *13*, 1604093.

T05. **Application of IR Spectroscopy to Study Thin Films of Biomolecules at the Electrified Metal-solution Interface**

Jacek Lipkowski

Department of Chemistry, University of Guelph, Ontario N1G 2W1, Canada

After a brief review of basic principles of the laws of reflection of light at interfaces, three methods of Infrared Reflection Absorption Spectroscopy (IRRAS) at electrified metal-solution interface will be discussed. The first is the subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) or in short potential difference IR spectroscopy. This technique finds application to study reversible adsorption of soluble molecules at electrode surfaces. Its principle will be described and methods of optimisation of the SNIFTIRS experiment will be discussed. Its application will be illustrated by the case of adsorption of adenine (a pyrimidine base) a gold electrode surface. The second technique to measure IR spectra at interfaces is the photon polarization modulation infrared reflection absorption spectroscopy (PM IRRAS). This technique is used to study films of insoluble molecules at various interfaces. I will discuss application of this technique to study model biological membranes containing antibiotic peptides supported at a gold electrode surface. The third technique is surface enhanced infrared reflection absorption spectroscopy (SEIRAS). I will describe principles of this method and will illustrate its application to study water structure in a model membrane supported at a gold electrode.

K09. Cytochrome *c* as Valuable Building Block in Multilayered Architectures of Biocatalysts on Electrodes

Fred Lisdat

Biosystems Technology, Institute of Applied Life Sciences, 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 more recently fructose dehydrogenase[2-4] or even 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. Two different pH optima are found for the reaction - at acidic and neutral pH. When one reaction partner - cyt c - is immobilized on a modified electrode, ET proceeds efficiently at neutral pH which can be concluded from well-shaped catalytic currents obtained in cyclic voltammetry. 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 surface plasmon resonance (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]. In order to study the effects which influence the self-exchange among different cyt c molecules a mutational study has been performed[6]. For this purpose 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 protein mutants has been verified by NMR and UV/Vis measurements. It can be shown that electro-active protein/silica nanoparticle multilayers are 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.

References

1. S. C. Feifel, A. Kapp, F. Lisdat in *Biosensors Based on Aptamers and Enzymes*, Springer: Berlin, **2014**, *140*, pp. 253-298.
2. F. Lisdat, R. Dronov, H. Möhwald, F. W. Scheller, D. G. Kurth *Chem. Comm.* **2009**, *3*, 274.
3. S. C. Feifel, A. Kapp, R. Ludwig, F. Lisdat *Angew. Chemie* **2014**, *126*, 5782.
4. C. Wettstein, K. Kano, D. Schäfer, U. Wollenberger, F. Lisdat *Anal. Chem.* **2016**, *88*, 6382.
5. K. R Stieger *et al. Nanoscale* **2016**, *8*, 10695.
6. S. C. Feifel, K. R. Stieger, A. Kapp *et al. ACS Omega* **2016**, *1*, 1058.

K10. Surface-immobilized Electrically Actuated DNA Layers for the Measurement of Binding Kinetics, Stokes Radius and Conformational Changes of Proteins

Wolfgang Kaiser, Friederike Möller, Ulrich Rant

Dynamic Biosensors GmbH, Martinsried, Germany
kaiser@dynamic-biosensors.com

Molecular interactions play a crucial role in all biological systems. Binding kinetics are of great importance to understand molecular interactions. Additionally, the conformation (e.g. at allosteric regulation) or oligomeric state (size) of the interacting partners often exhibit a pronounced effect on the binding affinity/avidity.

We present how self-assembled DNA monolayers actuated by electric fields can be utilized to measure binding kinetics and the hydrodynamic diameter of proteins on a chip. Using this approach conformational changes induced by small molecules can be detected.

DNA nano-levers immobilized to microelectrodes are functionalized with proteins. The negatively charged DNA nano-levers are actuated by alternating electric fields and thus the proteins are swayed through the solution above the surface at high frequencies.[1] The speed of this movement is measured optically by a fluorescence energy transfer from a fluorescent dye at the DNA's distal end to the surface in real-time. Since the switching speed depends on the hydrodynamic friction of the protein, the drag can be directly converted into a hydrodynamic diameter (Stokes diameter) of the protein.

We show analysis examples of conformational changes and allosteric regulation (kinases, STING, transglutaminase) as well as binding kinetics of challenging (multi-specific) binders.

References

1. A. Langer, P. A. Hampel, W. Kaiser, J. Knezevic, T. Welte, V. Villa, M. Maruyam, M. Svejda, S. Jähner, F. Fischer, R. Strasser, U. Rant *Nat. Commun.* **2013**, *4*, 2099.

SC06. Electrochemical Stability of Thiols and Disulfides Assembled on Gold in Physiological Medium

Adam Kolodziej, Carlos Guillen Posteguillo, Roshni Mistry,
Francisco Fernandez-Trillo, Paramaconi Rodriguez

School of Chemistry, University of Birmingham, B15 2TT, UK
axk595@bham.ac.uk

The importance of thiol-modified gold surfaces has been continuously investigated by the development of sensors[1], immobilized catalysts[2] and drug delivery strategies[3], with a substantial effort being focused on biomedical applications.

Electrochemistry has been widely applied in the field of sensors because its high sensitivity4 and recently the electrochemically-controlled delivery of drugs have also attracted the attention of researchers around the globe.[5] Therefore, electrochemical desorption of thiols is of interest since it determines the operational limits for the reliable sensor performance. On the other hand, it provides the conditions of a platform for a systematic drug delivery. While the electrochemical desorption of thiols from gold surfaces has been mainly studied in alkaline media using a range of techniques, only a few attempts have been conducted in neutral medium; and none of them in an electrolyte that mimics physiological conditions.[6]

In this work, we explore the electrochemical stability of thiol-modified electrodes in physiological medium. First, we investigate the stability of 4 different thiols: 3-mercaptopropionic acid, 2-mercaptoethanol, 1,4-dithiothreitol and thioctic acid on polycrystalline bead-electrodes using cyclic voltammetry (CV) and newly introduced progressive potential-step chronoamperometry. Subsequently, we study the impact of the crystalline structure of gold on the electrochemical desorption of thiols.

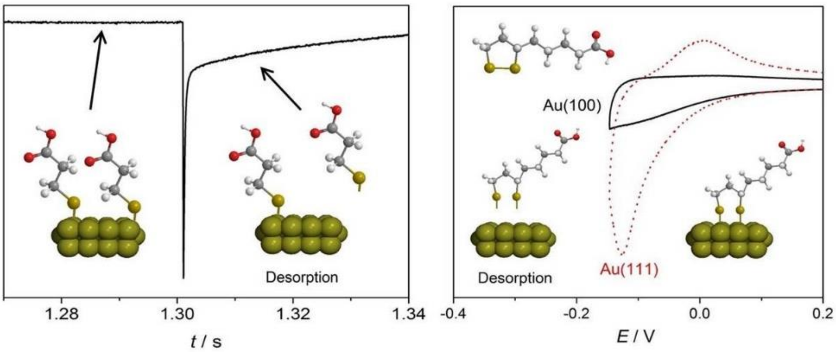


Figure 1. Chronoamperometric profile showing desorption of 2-mercaptoethanol from polycrystalline gold electrode (left panel). Voltammetric profiles showing desorption of thioctic acid from Au (111) (dotted line) and Au (100) (solid line) (right panel).

Our results indicate that SAMs of disulfides on gold electrodes are more stable than SAMs formed by thiols. We also report on the superior stability of the SAM on the Au(100) in comparison with the monolayers adsorbed on the Au(111) electrode.

References

1. D. Mandler, I. Turyan *Electroanalysis* **1996**, *8*, 207.
2. D. P. Wernette, C. Mead, P. W. Bohn, Y. Lu *Langmuir* **2007**, *23*, 9513.
3. P. Mali, N. Bhattacharjee, P. C. Searson *Nano Lett.* **2006**, *6*, 1250.
4. J. Monzo, I. Insua, F. Fernandez-Trillo and P. Rodriguez *Analyst* **2015**, *140*, 7116.
5. J. Wang, G. Rivas, M. Jiang and X. Zhang *Langmuir* **1999**, *15*, 6541.
6. E. Boubour and R. B. Lennox *Langmuir*, **2000**, *16*, 7464.

SC07. Straightforward Control of Chemical Surface Gradients by Wireless Electrochemistry

Gwendoline Tisserant,[a] Zahra Fattah,[b] Stéphane Reculusa,[a] Dodzi Zigah,[a]
Valérie Ravaine,[a] Alexander Kuhn,[a] Laurent Bouffier[a]

[a] *Institute of Molecular Sciences, Univ. Bordeaux, CNRS, Bordeaux INP, Talence, France*
[b] *Department of Chemistry, College of Science, Duhok University, Duhok, Iraq*
laurent.bouffier@enscbp.fr

The elaboration and characterization of surfaces or objects with sophisticated anisotropic features (i.e. *Janus* or patchy particles) is currently a very hot topic. In this context bipolar electrochemistry (BPE) is a convenient technique among the many available approaches. BPE is based on the polarization potential established on a conductive substrate immersed in an electrolyte and exposed to an electric field.[1,2] In fact, this polarization does evolve along the bipolar electrode and BPE is therefore well-suited for the conception of surface gradients.[3-5] Also, in contrast to conventional electrochemistry, BPE is wireless because there is no need for direct electric contacting the bipolar electrode. We report here the controlled generation of various physico-chemical gradients based on a variation of chemical composition, morphology or roughness. For that, various metals were deposited by BPE on several substrates exhibiting different geometries.[6,7] In particular, a series of results obtained with metal gradients on flat gold surfaces or cylindrical carbon fibers will be presented. Finally, the combination of electrode surface structuration introduced by a sacrificial template approach and the formation of a tunable molecular gradient by BPE was proposed.[8] In this case, the gradient involves the formation of a self-assembled monolayer on a gold surface by selecting an appropriate thiol molecule and subsequent reductive desorption by means of BPE. Under these conditions the remaining quantity of surface-immobilized thiol varies as a function of the axial position. This results in a dual physical/molecular gradient with original wetting properties.[8]

References

1. S. E. Fosdick, K. N. Knust, K. Scida, R. M. Crooks *Angew. Chem. Int. Ed.* **2013**, *52*, 10438.
2. L. Bouffier, D. Zigah, N. Sojic, A. Kuhn, Recent Advances in Bipolar Electrochemistry. In *Electroanalytical Chemistry: A Series of Advances*, *Vol. 27*, A. J. Bard and C. G. Zoski, Eds., CRC Press: Boca Raton, FL, **2017**, pp. 27-117.
3. S. Ramakrishnan, C. Shannon *Langmuir* **2010**, 26, 4602.
4. A. Lundgren, S. Munktell, M. Lacey, M. Berglin, F. Björefors *ChemElectroChem* **2016**, 3, 378.
5. Y. U. Kayran, V. Eßmann, S. Grützke and W. Schuhmann *ChemElectroChem* **2016**, *3*, 399.
6. G. Tisserant, Z. Fattah, C. Ayela, J. Roche, B. Plano, D. Zigah, B. Goudeau, A. Kuhn, L. Bouffier *Electrochim. Acta* **2015**, *179*, 276.
7. G. Tisserant, J. Gillion, J. Lannelongue, Z. Fattah, P. Garrigue, J. Roche, D. Zigah, A. Kuhn, L. Bouffier *ChemElectroChem* **2016**, *3*, 387.
8. L. Bouffier, S. Reculusa, V. Ravaine, A. Kuhn *ChemPhysChem* **2017**, DOI: 10.1002/cphc.201700398.

Sunday, November 5

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Mathieu Etienne and Gerd-Uwe Flechsig
09:00-09:40	T06	**Karsten Haupt** Micro and Nanofabricated Molecularly Imprinted Polymers for Bioanalysis, Biosensing and Bioimaging
09:40-10:00	K11	**Piyush Sindhu Sharma** Designed Electroactive Functional Monomers for Providing Desired Selectivity in Electrochemical Molecular Imprinting
10:00-10:15	SC08	**Carlo Gonzato** Molecularly Imprinted Films on Interdigitated Electrodes via Photo-iniferter Polymerization under Visible Light
10:15-10:30	SC09	**Zofia Iskierko** Epitope Imprinting for Selective Gluten Determination
10:30-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: Karsten Haupt and Alain Walcarius
11:00-11:40	T07	**Andrzej Lewenstam** Sensing Ion Fluxes Through Artificial and Biological Membranes and their Interfaces
11:40-12:00	K12	**Nicolas Plumere** Charge Recombination in Biophotoelectrodes
12:00-12:20	K13	**Karolien De Wael** Singlet Oxygen Based Electrosensing
12:20-12:35	SC10	**Serena Arnaboldi** Optimizing the Electrodeposition Protocol of Enantioselective Inherently Chiral Electrode Surfaces: a Multi-Technique Investigation
12:35-12:50	SC11	**Vitali Scherbahn** Wide-Field Surface Plasmon Microscopy for Detection of Biological Nano-/Microparticles
13:00-14:30		**Lunch**

14:30-15:45		**Afternoon session 1** Chairs: Andrzej Lewenstam and Karolien De Wael
14:30-14:50	K14	**Pawel Kulesza** Charge Propagation in Electroactive Materials: Diagnosis of Mechanisms and Dynamics with Microelectrochemical Devices
14:50-15:10	K15	**Gidi Shani** Sensors for Breath Testing: From Nanomaterials and Surface Modifications to Comprehensive Disease Detection
15:10-15:30	K16	**Sławomir Sęk** Activity of Lipopeptides Toward Biomimetic Lipid Films
15:30-15:45	SC12	**Mariano Garcia-Soto** Polymer-coated Gold Nanoparticles

15:45- **Social program**

20:00-22:00 **Dinner/Banquette**

T06. Micro and Nanofabricated Molecularly Imprinted Polymers for Bioanalysis, Biosensing and Bioimaging

Karsten Haupt, Frank Bokeloh, Paulina Rangel

Sorbonne Universités, Université de Technologie de Compiègne, Compiègne, France
karsten haupt@utc.fr

Biomimicry is the general term covering any approach aimed at reproducing artificially essential properties of one or more biological systems. This is done in order to exploit natural mechanisms or materials for direct applications in different technological domains, in particular in materials science. At the molecular level, one example of biomimetic materials is molecularly imprinted polymers (MIPs), also known as 'plastic antibodies'.

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

We present new approaches allowing for the synthesis of MIP by controlled/living radical polymerization and spatially controlled localized photopolymerization. This allows for example to obtain protein-size, soluble MIP nanogels with a homogeneous size distribution.[2] They show specific binding of their targets, small organic molecules or proteins,[3] with a nanomolar affinity and a good selectivity. Since MIPs are compatible with standard micro and nanofabrication techniques, they can also be obtained in any other physical form, and at the same time interfaced with other materials including transducers. The use of these functional nanomaterials for chemical and biosensing,[4-8] and for cell and tissue imaging[9] will be discussed.

Acknowledgments
We acknowledge financial support by the EU H2020 project NOSY (Grant Nr. 653839).

References

1. K. Haupt, A.V. Linares, M. Bompart, B. Tse Sum Bui *Top. Curr. Chem*. **2012**, *325*, 1.
2. P. Çakir, A. Cutivet, M. Resmini, B. Tse Sum Bui, K. Haupt *Adv. Mater*. **2013**, *25*, 1048.
3. S. Ambrosini, S. Beyazit, K. Haupt, B. Tse Sum Bui *Chem. Commun*. **2013**, *49*, 6746.
4. M. Bompart, Y. De Wilde, K. Haupt *Adv. Mater.* **2010**, *22*, 2343.
5. X-A. Ton, B. Tse Sum Bui, M. Resmini, P. Bonomi, I. Dika, O. Soppera, K. Haupt *Angew. Chem. Int. Ed.* **2013**, *52*, 8317.
6. Y. Fuchs, O. Soppera, A. G. Mayes, K. Haupt *Adv. Mater.* **2013**, *25*, 566.
7. C. Ayela, G. Dubourg, C. Pellet, K. Haupt *Adv. Mater*. **2014**, *26*, 5876.
8. L.P. Chia Gomez, A. Spangenberg, X. Ton, Y. Fuchs, F. Bokeloh, J. Malval, B. Tse Sum Bui, D. Thuau, C. Ayela, K. Haupt, O. Soppera *Adv. Mater*. **2016**, *28*, 5931.
9. M. Panagiotopoulou, Y. Salinas, S. Beyazit, S. Kunath, L. Duma, E. Prost, A.G. Mayes, M. Resmini, B. Tse Sum Bui, K. Haupt *Angew. Chem. Int. Ed.* **2016**, *55*, 8244.

K11. Designed Electroactive Functional Monomers for Providing Desired Selectivity in Electrochemical Molecular Imprinting

Piyush Sindhu Sharma,[a] Zofia Iskierko,[a] Maciej Cieplak,[a] Agnieszka Wojnarowicz,[a]
Wojciech Lisowski,[a] Krzysztof Noworyta,[a] Francis D'Souza,[b] and Wlodzimierz Kutner[a,c]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences,*
Kasprzaka 44/52, 01-224 Warsaw, Poland
[b] *Department of Chemistry, University of North Texas, Denton, 1155,*
Union Circle, #305070 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
psharma@ichf.edu.pl

Natural receptors offer the desired high selectivity or even specificity in recognition of target biomolecular compounds, when applied in biosensing. However, their instability under measurement conditions and low durability prompted researchers toward devising different artificial receptor alternatives. An emerging alternative approach suggests the use of "plastic antibodies" as the replacement for traditional biological receptors in sensing.[1] The number of designs and syntheses of biomimetic receptor systems capable of binding target analytes with affinity and selectivity similar to those of natural receptors is rapidly growing.[2-3] Importantly, these materials are used as recognition units for devising selective chemical sensors. Molecularly imprinted polymers (MIPs)[4] represent an excellent example of synthetic systems that mimic the recognition encountered in animated nature. These "**smart materials**" can selectively and reversibly bind only the target analyte because of the presence of dedicated imprinted molecular cavities in the polymer structure. Therefore, by choosing a starting material of proper recognition functionalities, one may succeed in fabricating molecular cavities in synthetic materials with the desired selectivity. Noticeably, formation of a stable pre-polymerization complex is important for preparation of a highly selective MIP.

Electrochemical detection systems based on microchip platforms are recently becoming popular for implementing field-portable devices.[5] These easy-to-use and sensitive analytical tools are necessary for detecting very low concentrations of the target analyte of the health care importance.[6]

Towards attaining this goal, we deposited in the present work the devised MIP synthetic receptor in the form of a thin film on a commercial Au disk thin-film electrode surface. Then, this MIP coated Au electrode was assembled in an electrochemical microcell to construct a microfluidic platform. Capacitive impedimetry was applied to determine biomarkers through reversible binding by dedicated molecular cavities of the MIP synthetic receptor. The present work will present an easy and effective way of conductive MIP film preparation and its use as the recognition unit in a microfluidic based impedimetric sensing device.

References

1. K. Haupt, K. Mosbach. *Trends Biotechnol.* **1998,** *16*, 468.
2. P. S. Sharma, A. Pietrzyk-Le, F. D'Souza, W.Kutner *Anal. Bioanal. Chem.* **2012,** *402*, 3177.
3. P. S. Sharma, Z. Iskierko, A. Pietrzyk-Le, F. D'Souza, W. Kutner *Electrochem. Commun.* **2015**, *50*, 81-87.
4. P. S. Sharma, M. Dabrowski, F. D'Souza, W. Kutner *Trac-Trend Anal Chem* **2013**, *51*, 146.
5. G. M. Birnbaumer, P. A. Lieberzeit, L. Richter, R. Schirhagl, M. Milnera, F. L. Dickert, A. Bailey, P. Ertl *Lab Chip* **2009,** *9*, 3549.
6. C-H. Weng, W.-M. Yeh, K.-C. Ho, G. B. Lee *Sens. Actuators B* **2007**, *121*, 576.

SC08. Molecularly Imprinted Films on Interdigitated Electrodes *via* Photo-iniferter Polymerization under Visible Light

Carlo Gonzato, Nadja Leibl, Ioanna Teresa Gad, Léa Ledaine, Karsten Haupt

[a] *Sorbonne Universitės, Compiegne University of Technology, Compiegne, France*
carlo.gonzato@utc.fr

Molecularly imprinted polymers (MIPs) are synthetic materials obtained by polymerization in presence of molecular templates, which feature binding sites with recognition properties on a par with those of antibodies, hormone receptors and enzymes.[1]

Mostly made of poly(meth)acrylates, MIPs have superior physico-chemical properties compared to their natural counterparts, which make them perfectly suited for technological applications wherein a recognition process is involved. Thanks to their easy engineering, MIPs are available in different physical formats and can be interfaced with a variety of different supports.[2] Their range of applications goes from solid phase extraction to affinity separation, immunoassays, tissue imaging and biochemical sensing.[3]

In this contribution, we show an easy approach for the *in situ* synthesis of molecularly imprinted films *via* visible-light, photo-iniferter polymerization.[4-5] Upon grafting of a trithiocarbonate onto amino-modified glass slides, blue light from a LED was used to grow a thin film of poly(methacrylamide-co-trimethylolpropane trimethacrylate) imprinted against trimesic acid as model template. This approach was further optimized with the functionalization of an interdigitated electrode where the polymer layer targeted exclusively the metal part of the electrode.

References

1. K. Haupt, *Molecular Imprinting, Springer: Berlin*, **2012**, 1-28.
2. S. Beyazit, B. Tse Sum Bui, K. Haupt, C. Gonzato *Prog. Polym. Sci.* **2016**, *62*, 1.
3. C. Alexander, H. S. Andersson, L. I. Andersson, R. J. Ansell, N. Kirsch, I. A. Nicholls, J. O'Mahony and M. J. Whitcombe *J. Mol. Recognit.* **2006**, *19*, 106.
4. J. Xu, S. Shanmugam, N. A. Corrigan, C. Boyer, *Progress in Controlled Radical Polymerization: Mechanisms*, Washington DC, **2015**, *1187*, 247-267.
5. M. J. Garcia-Soto, K. Haupt, C. Gonzato *Polym. Chem.* **2017**, *8*, 4830.

SC19. Epitope Imprinting for Selective Gluten Determination

Zofia Iskierko,[a] Piyush S. Sharma,[a] Maciej Cieplak,[a] Alessandra Bossi,[b]
Krzysztof Noworyta,[a] Francis D'Souza,[c] Wlodzimierz Kutner,[a,d]

[a] *Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, Poland*
[b] *Department of Biotechnology, University of Verona, Verona, Italy*
[c] *Department of Chemistry,University of North Texas, Denton, Texas, USA*
[d] *Faculty of Mathematics and Natural Sciences,*
Cardinal Stefan Wyszynski University in Warsaw, Warsaw, Poland

Gluten is the allergen that triggers autoimmune reactions in people suffering of celiac sprue (CS). CS, also known as gluten enteropathy is, after hypolactasia, the second most common food intolerance. It is estimated that CS affects the 1-2 % of the European population with direct costs on the healthcare estimated about 3 bn Euros/year.[1] The only effective therapy is strict dietary abstinence from gluten. Even a small contamination of food with gluten can cause serious adverse reactions from digestive system. Food contain less than 20 mg/kg of gluten is considered as "gluten-free" and can be eaten safely. MIPs have a long history dating back to early 1930s.[2] They are artificially made receptors with the ability to bind reversibly and to recognize the target analytes. Although fabrication of a MIP against small molecules or peptides is now straightforward, imprinting of large molecular structures, such as proteins and other biomacromolecules, is still challenging.[3,4] Among other approaches, epitope imprinting,[5] have been developed to overcome problems related to imprinting of macromolecules.

In the current study, a toxic gluten epitope, PQQPFPQQ, was chosen as a template for imprinting. The MIP film was prepared by electrochemical polymerization of bis(bithiophene) derivatives, bearing either cytosine or carboxylic acid substituent, in the presence of the template and a cross-linker. After deposition, the template was extracted from the polymer film. Subsequently, the film composition was characterized by X-ray photoelectron spectroscopy (XPS) as well as its morphology and thickness were studied by scanning electron (SEM) and atomic force (AFM) microscopy. Finally, analytical parameters of the devised chemosensor for epitope detection were evaluated.

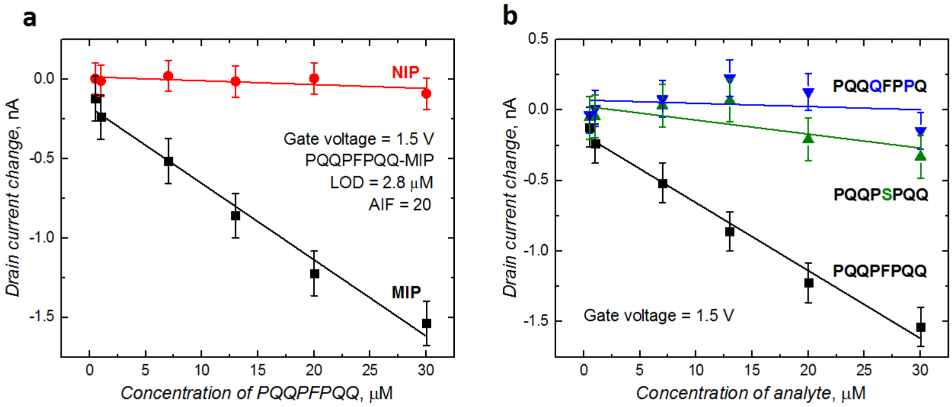


Figure 1. Preliminary results of gluten epitope in buffer (pH≈7) determination using extended-gate field-effect transistors (EG-FETs) as transducers. (a) Calibration curves for the gluten epitope on the MIP and NIP film-coated EG-FETs. (b) Comparison of calibration curves of similar epitopes on MIP film-coated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

References

1. K. H. Long, A. Rubio-Tapia, A.E.Wagie *et al. Aliment. Pharmacol. Ther.* **2010**, *32*, 261.
2. M. V. Polyakov, *Zh. Fiz. Khim.* **1931**, *2*, 799.
3. M. J. Whitcombe, N. Kirsch, I.A. Nicholls *J. Mol. Recognit.* **2014**, *27*, 297.
4. A. Bossi, F. Bonini, A. P. Turner, S. A. Piletsky *Biosens. Bioelectron.* **2007**, *22*, 1131.
5. A. M. Bossi, P.S. Sharma, L. Montana, G. Zoccatelli, O. Laub, R. Levi *Anal. Chem.* **2012**, *84*, 4036.

T07. Sensing Ion Fluxes Through Artificial and Biological Membranes and their Interfaces

Andrzej Lewenstam [a,b]

[a] *AGH University of Science and Technology, Faculty of Materials Science and Ceramics,*
al. Mickiewicza 30, Kraków 30-059, Poland
[b] *Åbo Akademi University, Center for Process Analytical Chemistry and Sensor Technology 'ProSens',*
Biskopsgatan 8, Turku 00410, Finland
andrzej.lewenstam@abo.fi

Ion flux through a membrane surface (membrane-solution interface) is the condition of every electrochemical ion-sensitivity. This condition applies both to ion-selective membrane electrodes (ISEs) and biological membranes. In the field of ISEs, the transport of ions determines the electrochemical concentration-dependent signals. Ion transport through biological membranes is of vital importance for homeostasis of living organisms, in particular in neuronal signals and energy release.

The key application area of ISEs is in clinical chemistry, where routine measurements that are fast, inexpensive, reliable, service-free, and fully automated are of importance[1]. Today, ISEs are widely and routinely used for the determination of electrolytes (K^+, Na^+, Cl^-) and pH in physiological fluids such as whole blood, serum, plasma or urine. In routine measurements, in hospital laboratories, flow-through ISEs are used, which allow for measurements in a drop-like sample volume (about 30 microliters) within a few seconds.

For measurements with biological membranes, the flow-through ISEs known from clinical applications were 3D-redesigned and placed on one flat surface to form a platform that can fit the cup with living bronchial epithelial cells. Two platforms work in proximity of the cells' surfaces, basolateral and apical. In this way, the measurements in a small volume of solution (about 10 microliters) that bathes the cells for over a few hours was continuously performed.[2]

The tutorial shows how to formally (mathematically) characterize the ion fluxes and derive patterns of the membranes' electrochemical responses using a Nernst-Planck-Poisson model (NPP).[3] The membrane surfaces modified by ion concentration gradients over the membranes and the fluxes controlled by different primary to interfering concentration ratios or blockers of ion channels will be considered. The NPP will be presented as a gateway for practical realizations such as optimizing the performance of ion-selective electrode platforms, measurements in one-drop of blood, and characterization of ion-fluxes through a living endothelial cell layer.

Acknowledgements

National Science Centre (NCN, Poland) financial support via research grant no. 2014/15/B/ST5/02185 is acknowledged.

References

1. A. Lewenstam *Electroanalysis* **2014**, *26*, 1171.
2. M. Zajac, A. Lewenstam, K. Dolowy *Bioelectrochem.* **2017**, *117*, 65.
3. K. Szyszkiewicz, J. J. Jasielec, M. Danielewski, A. Lewenstam, R. Filipek *J. Electrochem. Soc.* **2017**, *164*, E3559.

K12. Charge Recombination in Biophotoelectrodes

Nicolas Plumeré

Ruhr-Universität Bochum, Center for Electrochemical Sciences, Bochum, Germany
Nicolas.plumere@rub.de

The integration of photosynthetic proteins in biophotoelectrodes is envisioned for the production of electricity[1] or chemical fuels. To this end, redox hydrogels proved particularly suitable as matrices for the immobilization and electrical contacting of various photosynthetic proteins to electrodes. We tuned the redox potentials of the electron relays and the properties of the polymeric supporting matrix to enable benchmark photocurrent densities (300 μA cm^{-2} for PS1 [2] and up to 400 μA cm^{-2} for PS2 [3]) at low overpotential.[4] In analogy to the working principle of dye sensitized solar cells, an important feature of biohybrid solar cells for conversion of light to electricity is the charge carriers needed for collection of the high-energy electron from the photosystem.[5] The main limitation in energy conversion efficiency is the recombination of this charge carrier at the photoelectrode, a process that decreases both the photocurrent and the open circuit voltage. Moreover, this charge recombination process is suspected to induce degradation of the photosynthetic protein.[6] We demonstrate that the hydrogel film properties as well as the electrode surface chemistry can be tuned to minimize the various charge recombination pathways. This concept opens up the possibility to build biohybrid photovoltaics free of semi-conductor materials.

Acknowledgements
Financial support by the Cluster of Excellence RESOLV (EXC 1069), by the ERC starting grant 715900 and by the ANR-DFG project SHIELDS (PL 746/2-1) is gratefully acknowledged.

References

1. N. Plumeré *Nat. Nanotechnol.* **2012**, *7, 616.*
2. T. Kothe, S. Pöller, F. Zhao, P. Fortgang, M. Rögner, W. Schuhmann, N. Plumeré *Chem. – Eur. J.* **2014**, *20*, 11029.
3. K. Sokol, D. Mersch, V. Hartmann, J. Z. Zhang, M. M. Nowaczyk, M. Rögner, A. Ruff, W. Schuhmann, N. Plumeré, E. Reisner *Energy Environ. Sci.* **2016**, *9*, 3698.
4. V. Hartmann, T. Kothe, S. Pöller, E. El-Mohsnawy, M. M. Nowaczyk, N. Plumeré, W. Schuhmann, M. Rögner *Phys. Chem. Chem. Phys.* **2014**, *16*, 11936.
5. M. M. Nowaczyk, N. Plumeré in *Advances in Biochemical Engineering/Biotechnology, Biophotoelectrochemistry of Photosynthetic Proteins*, Springer International Publishing: Cham, **2016**, pp. 111-136.
6. M. M. Nowaczyk, N. Plumeré *Nat. Chem. Biol.* **2016**, *12*, 990.

K13. Singlet Oxygen Based Electrosensing

Karolien De Wael,[a] Stanislav Trashin,[a] Vanoushe Rahemi,[a]
Karpagavalli Ramji,[b] Liselotte Neven,[a] Sergiu Gorun[b]

[a] AXES Research Group, Department of Chemistry, University of Antwerp,
Groenenborgerlaan 171, 2010 Antwerp, Belgium
[b] Department of Chemistry and Biochemistry and the Center for Functional Materials,
Seton Hall University, 07079 New Jersey, USA
karolien.dewael@uantwerpen.be

It is well known that phenolic compounds and, particularly, hydroquinone can shuttle electrons between horse radish peroxidase (HRP) and an electrode, which allows the bioelectrocatalytical reduction of H_2O_2 by the enzyme. When a phenolic compound shuttles the electrons, it passes through many cycles of oxidation and electrochemical reduction (regeneration) near the electrode. Such mechanism enhances the electrochemical response of the compound and has been employed for the electrochemical detection of phenols and their derivatives. However, H_2O_2 as an oxidant must be introduced into the system, which is an obvious limitation of the method. Our solution is to replace the enzyme with a photosensitizer which produces reactive oxygen species and can catalyze the oxidation of a compound of interest by O_2 that is naturally present in the measuring conditions. Here we used a fluorinated phthalocyanine complex of Zn which is capable to form singlet oxygen under red light illumination (λ ca. 650 nm).

Figure 1 illustrates the electrochemical behavior of hydroquinone at a graphite screen-printed electrode modified by TiO_2 impregnated with a fluoroalkylated zinc phthalocyanine ($F_{64}PcZn$). Introduction of hydroquinone in the measuring buffer results in the reversible redox process at proximately 0.05 V. Under illumination with a red LED laser, the reduction current increased and the cyclic voltammogram transformed into a wave shaped curve in the same way as expected for an electrocatalytical mechanism. In contrast to bioelectrocatalysis with enzymes, the reaction includes the photosensitizer, which under the light illumination catalyzes the oxidation of hydroquinone by oxygen. The advantage is that the catalysis process is switched by light, and the oxidation of hydroquinone does not require hydrogen peroxide. The regulation by light admits of careful subtraction of the background in amperometry measurements, which facilities quantitative detection of a phenolic compound of interest.

Singlet oxygen is known to be a strong oxidant agent which is responsible for photochemical degradation of phenol and phenolic compounds including pollutants and pharmaceuticals. The antibiotic amoxicillin contains a 4-hydroxyphenyl moiety coupled to a penicillin core structure. Thus, it is considered as an important analyte, which can be detected by the described above method. At least two factors define the successful detectability of a compound in the described system: (1) oxidation kinetics under light illumination and (2) reduction kinetics of the formed derivative at the electrode.

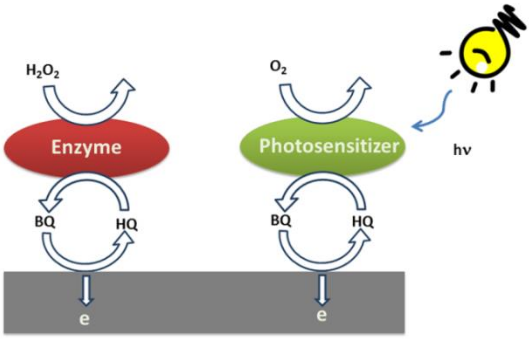


Figure 1.

References

1. S. Trashin, V. Rahemi, K. Ramji, L. Neven, S. M. Gorun, K. De Wael *Nat Commun.* **2017**, *8*: 16108.

SC10. Optimizing the Electrodeposition Protocol of Enantioselective Inherently Chiral Electrode Surfaces: a Multi-Technique Investigation

Patrizia Mussini,[a] Claudia Malacrida,[a] Mirko Magni,[a] Alessio Orbelli Biroli,[b] Tiziana Benincori,[c]
Silvia Cauteruccio,[a] Francesco Sannicolò,[a] Serena Arnaboldi[a]

[a] *Università degli Studi di Milano, Dipartimento di Chimica, Milano, Italy*
[b] *CNR-ISTM, Milano, Italy*
[c] *Università degli Studi dell'Insubria, Como, Italy*
serena.arnaboldi@unimi.it

We have recently introduced[1-2] "inherently chiral" enantiopure electrode surfaces of outstanding chirality manifestations, including circularly polarized luminescence, reversibly potential-driven circular dichroism, and large potential differences for the enantiomers of chiral probes in voltammetry experiments performed on such surfaces.

The outstandingly powerful "inherent chirality" concept implies a molecular structure where the stereogenic element does not consist in an isolated stereocentre or an external chirality source, but originates from a tailored torsion in the whole main backbone endowing the molecule with its key functional property (here electroactivity).

A key issue is now to investigate the enantioselection mechanism and to optimize the experimental protocols for the deposition of our inherently chiral surfaces. For both aims it is important to study the thickness and regularity of the chiral oligomer films as a function of the experimental conditions. We started a systematic profilometry study correlated to electrochemical impedance spectroscopy measurements of the oligomer films obtained by carefully controlled electrodeposition, varying one by one different experimental parameters. The study is also important to properly compare enantioselection by films prepared from different inherently chiral monomers, including e.g. bisindole and tetrathiahelicene ones.

References

1. F. Sannicolò, S. Arnaboldi, T. Benincori, V. Bonometti, R. Cirilli, L. Dunsch, W. Kutner, G. Longhi, P. R. Mussini, M. Panigati, M. Pierini, S. Rizzo *Angew. Chem. Int. Ed.* **2014**, *53*, 2623.
2. S. Arnaboldi, P. Mussini, M. Magni, F. Sannicolò, T. Benincori, R. Cirilli, K. Noworyta, W. Kutner *Chem. Sci.* **2015**, *6*, 1706.

SC11.

Wide-Field Surface Plasmon Microscopy for Detection of Biological Nano-/Microparticles

Vitali Scherbahn, Shavkat Nizamov, Vladimir M. Mirsky

Department of Nanobiotechnology, Institute for Environment and Natural Science, Brandenburgische Technische Universität Cottbus-Senftenberg, 01968 Senftenberg, Germany
vitali.scherbahn@b-tu.de

Biological nano- (NPs) and microparticles (MPs) belong to our everyday life. In many cases, these species may also possess a dangerous impact on human and animal health. Therefore, fast, cost-efficient, and direct methods for detection, investigation and ultra-sensitive quantification of biological NPs and MPs are required. In this work, we present a new approach for detection, visualization, and quantification of microorganisms. The approach was tested using *E. coli K12*, *S. cerevisiae* and an additional application of biological NPs – exosomes, which are considered to be highly promising cancer markers.[1] The method is based on surface plasmon microscopy (SPM) enabling ultra-sensitive, label-free detection and visualization of small local changes of refractive index near the sensor surface.[2] Examples of SPM application for detection of bacterial and yeast cells are shown in Fig. 1. Surface coatings with different hydrophobicity and electrostatic properties were applied to vary the affinity properties of the biological objects. Concentration dependencies were studied. Taking into account a reasonable detection rate as one NP/MP per 10 s, we obtain a limit of detection of 105-106 species/ml. Notably, our detection method is very stable against impurities and can be applied in very complex media.[3]

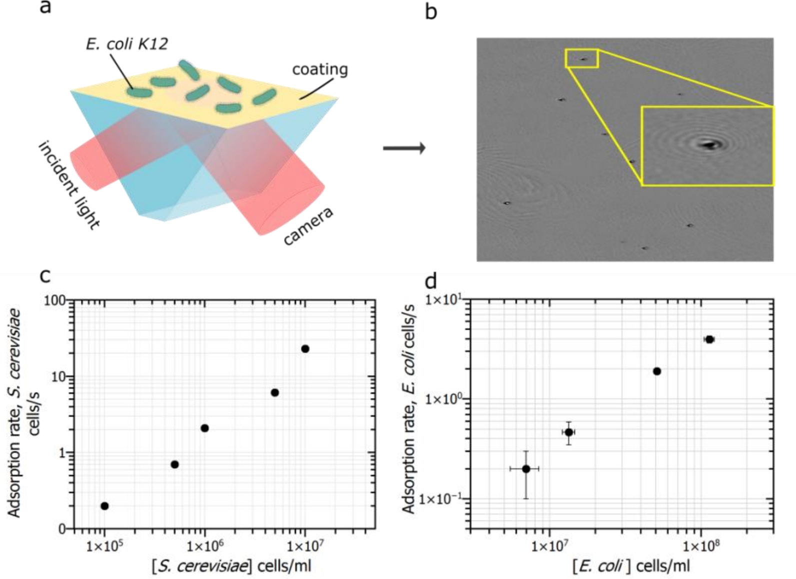


Figure 1. (a) Schematic set-up for detection of bacteria cells using surface plasmon microscopy (SPM). (b) Real-time differential SPM image visualizing single bacteria cells on coated surface and a highlighted zoomed-in SPM signal of a single *E. Coli K12* cell (inset). Adsorption rate of *S. Cerevisiae* (c) and *E. Coli K12* (d) in dependence to the concentration

References

1. J. Webber, T. C. Stone, E. Katilius, B. C. Smith, B. Gordon, M. D. Mason, Z. Tabi, I. A. Brewis, A. Clayton *Mol. Cell. Proteomics* **2014**, *13*, 1050.
2. V.Scherbahn, S. Nizamov, V. M Mirsky *Microchim. Acta* **2016**, *183*, 2837.
3. S. Nizamov, V. Scherbahn, V. M. Mirsky *Anal. Chem.* **2017**, *89*, 3873.

K14. Charge Propagation in Electroactive Materials: Diagnosis of Mechanisms and Dynamics with Microelectrochemical Devices

Pawel J. Kulesza, Iwona A. Rutkowska, Krzysztof Miecznikowski

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

Historically, electrochemistry in the absence of a bulk liquid phase has focused on the problems of energy storage and production. Recently, it has become possible to apply conventional electrochemical methods to characterize solid-state type redox electrolytes with respect to analytical characterization of materials, measurement of electron transfer rates, and determination of analytes using amperometric sensing. The characterization of materials by solid-state voltammetry primarily has focused on mixed-valence, ionically conducting compounds and on diverse organic ionomers hosting identifiable molecular (redox) sites.

We are going to address practical issues related to the principles and analytical aspects of electrochemical studies (typically done at room temperature) of solid, rigid or semi-rigid (nonfluid) systems in the absence of a liquid solution phase. Representative examples include redox and conducting organic polymers, melts and solid solutions of redox centers in solid ionic conductors, mixed-valence polynuclear inorganic materials, transition metal salts, oxides, and zeolites. The emphasis is on the elements of dynamics for the efficient delivery of charge and on reactivity of the ‘redox conducting’ materials. The effective (apparent) diffusional mechanism is critical to the success of most analytical measurements in solid-state.

The potential materials for solid-state electrochemical measurements are expected to contain three-dimensionally distributed highly concentrated redox centers between which fast electron self-exchange (hopping) is feasible. These redox centers are fixed and, although they may have short range mobility about an equilibrium position, they classically are macroscopically immobile. The applicable materials also must host mobile counter-ions that are capable of providing charge balance during electron transfers, thereby serving the same purpose as the supporting electrolytes in conventional electrochemistry. The population of these ions must be sufficient to support diffusive mass transport of electrons and to minimize ohmic effects.

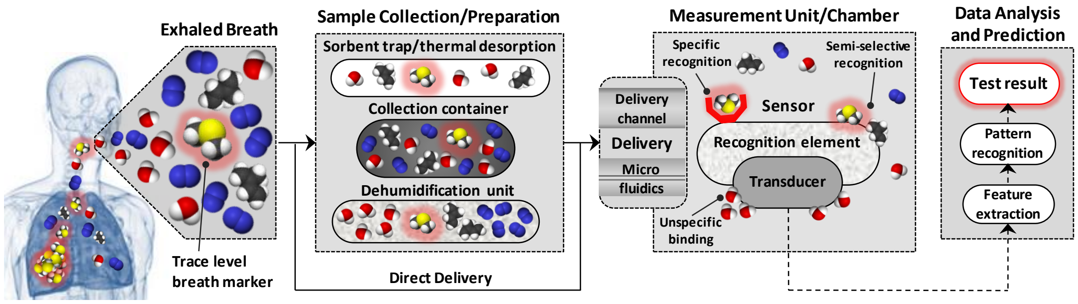
We will describe typical electrochemical cells and experimental tactics to overcome the relatively slow dynamics of transport in solid (non-fluid) systems. Application of microdimensional electrodes leads to an improvement in the quality of solid-state electrochemical data and provides new diagnostic and analytical possibilities. Basic concepts of mechanistic studies, which are relevant to the development of novel analytical methods, together with trends towards possible future applications will also be addressed.

K15. Sensors for Breath Testing: From Nanomaterials and Surface Modifications to Comprehensive Disease Detection

Gidi Shani

The Department of Chemical Engineering and Russell Berrie Nanotechnology Institute,
Technion – Israel Institute of Technology, Haifa 3200003, Israel

The analysis of volatile organic compounds in exhaled breath samples represents a new frontier in medical diagnostics because it is non-invasive and potentially inexpensive. Several advances in the knowledge and development of sensors must occur before breath testing can become a clinical reality. Sensing matrices based on nanomaterials are likely to become a clinical and laboratory diagnostic tool because they are significantly small, easy-to-use, and inexpensive. An ideal nanomaterial-based sensor for analyzing volatile organic compounds should be sensitive at very low analyte concentrations in the presence of environmental or physiological confounding factors. It should also respond rapidly and differently to small changes in concentration and provide a consistent output that is specific to a given exposure. When not in contact with the analyte, the sensor should quickly return to its baseline state or be simple and inexpensive enough to manufacture large numbers of disposable units.



The talk pays attention to the technological gaps and confounding factors related to nanomaterial sensor-based breath testing, in the hope of directing future research and development efforts towards the best possible approaches to overcoming these obstacles. The talk discusses breath testing as a complex process involving numerous steps, each of which has various possible technological alternatives with advantages and drawbacks that might affect the performance of the nanomaterial-based sensors that lie at the heart of the breath testing system. With this in mind, different ways to choose nanomaterial-based sensors and the related surface modifications are discussed, while considering the profile of the targeted breath markers and the possible limitations of the applied sensing approach, and going hand in hand with the choice of the surrounding breath-testing setup. The talk will also discuss how the dynamic range and selectivity of the applied sensors can be tailored to detect pre-evaluated breath and disease-related volatile organic compounds. Based on these aspects, the account will describe the benefits and implications of using nanomaterial-based sensors for breath testing and suggest ways to overcome these obstacles, either through approaches concerning the improvement of the sensing elements or through supporting techniques such as preconcentration and dehumidification techniques.

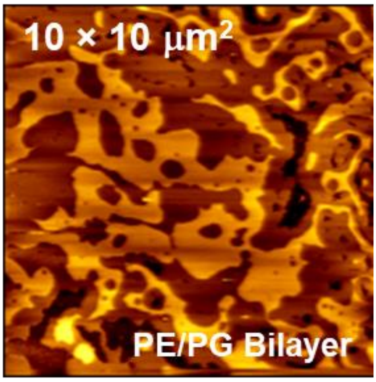
K16. Activity of Lipopeptides Toward Biomimetic Lipid Films

Sławomir Sęk, Joanna M. Wenda, Joanna Juhaniewicz-Dębińska,
Dagmara Tymecka, Dorota Konarzewska

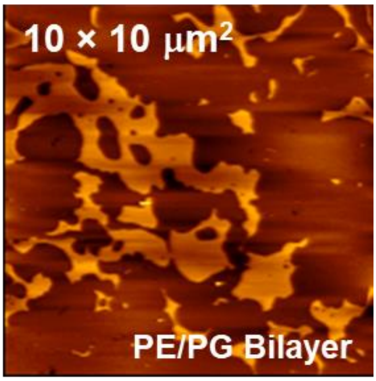
Biological and Chemical Research Centre, Faculty of Chemistry, University of Warsaw,
Żwirki i Wigury 101, 02-089 Warsaw, Poland
slasek@chem.uw.edu.pl

The increasing resistance of bacteria to available antibiotics has become major clinical problem worldwide. This situation creates the need to develop new antibiotics with new modes of action. The group of compounds that meet these criteria include lipopeptides. In contrast to conventional antibiotics, which act on specific targets such as enzymes involved in cell wall synthesis or DNA, many lipopeptides have ability to penetrate and destroy the cell membrane, leading to its irreversible damage.[1] Since their action in many cases seems to be less specific comparing to traditional drugs, microbial resistance may occur with lower probability. Therefore, lipopeptides are seriously considered as promising new class of antibiotics. Although the bactericidal activity of these compounds was reported in numerous publications, the detailed mechanisms of their interactions with bacterial membranes still remain unclear. Undoubtedly, better understanding of the nature of molecular interactions which determine the activity of lipopeptides is necessary for further effective development of new drugs.

Before exposure to lipopeptide



After exposure to lipopeptide



Due to the complex nature of bacterial cell membranes, biomimetic lipid films are often considered as their simplified models.[2] These include inner plasma membrane of either Gram-positive and Gram-negative bacteria and outer membrane of Gram-negative bacteria. In our work, we have employed Langmuir technique and atomic force microscopy (AFM) to investigate the interactions of several novel lipopeptides synthesized in our laboratory with negatively charged phospholipid films. The latter served as a simplified models of inner membrane of Gram-negative bacteria.[3] It was found that the activity of lipopeptides toward biomimetic membranes can be controlled by several factors including charge and chirality of amino acids and the length of lipophilic chain which is covalently coupled to N-terminus of peptide moiety. Interestingly, the effective size of the peptide portion of the molecules seem to determine ability of the lipopeptide to insert into the lipid membrane. We have also found that insertion of the lipopeptides into the model membranes strongly alters lateral distribution of the membrane components and leads to its substantial fluidization as demonstrated in attached AFM images. The dynamics of reorganization was noticeably faster in the presence of lipopeptide with smaller size of peptide moiety, however, it depends also on length of lipophilic hydrocarbon chain.

References

1. M. L. Nelson, M.C. Grier, S. E Barbaro, M.Y. Ismail, *Anti-Infect. Agents Med. Chem.* **2009**, *8*, 3.
2. J. Lipkowski *Phys. Chem. Chem. Phys.* **2010**, *12*, 13874.
3. J. Wenda, J. Juhaniewicz, D. Tymecka, D. Konarzewska, S. Sęk *Langmuir* **2017**, *33*, 4619.

SC12. Polymer-coated Gold Nanoparticles

Garcia-Soto M., Gonzato C., Haupt K.

Sorbonne Universités, Université de Technologie de Compiègne,
CNRS Laboratory for Enzyme and Cell Engineering,
CS 60319, 60203 Compiègne Cedex, France
mariano.garcia-soto@utc.fr

Gold nanoparticles (GNP) display intense colorations in the visible spectrum when illuminated. This effect is due to their localized surface plasmon resonances (LSPR), which mainly depend on the characteristics of the particles, but also on minimal changes on their interface; therefore making them attractive platforms for sensing. Given their unique properties, their applications range from electronics, catalysis, and as probes for diagnostics and therapeutic agents.

Molecularly imprinted polymers (MIP) are synthetic receptors obtained by co-polymerizing interacting and cross-linking monomers around a target template. MIPs contain binding sites with affinities analogous to biological receptors, but are more stable, easy to prepare, and inexpensive. They are typically produced by thermal- or photo-induced radical polymerizations, with novel methods producing composites on nanoparticles for potential medical applications.[1, 2]

GNP can be designed to absorb more light than scatter it, with excess energy released as heat in the vicinity of their surface. By locally inducing photo-thermally initiated polymerizations on their surface, our aim is to fabricate thin polymer coatings on them to develop into molecularly imprinted polymer composites for the direct detection of target compounds by surface-enhanced Raman spectroscopy.[3]

GNP and silver colloids, in particular their aggregates or seeded-growth, have been reported to provide a notable enhancement of the Raman signal, but also of troublesome reproducibility.[4] Our approach relies on having immobilized nanoparticles, uniformly distributed at high density, with polymer coatings in the nanometer range to bind and quantify target molecules.

We have observed polymers being formed around GNP as result of photo-thermally inducing free-radical polymerizations with light matching the wavelength of their maximum absorption. This includes the red-shift and broadening of their LSPR and increased particle sizes. We also have produced supports homogeneously decorated with GNP having polymer coatings produced on them. We are now working on controlling the thickness of these polymers to improve their sensing capacity.

References

1. S. Beyazit, S. Ambrosini, N. Marchyk, E. Palo, V. Kale, T. Soukka, B. Tse Sum Bui, K. Haupt *Angew. Chem., Int. Ed.* **2014**, 126, 9065.
2. M. Panagiotopoulou, Y. Salinas, S. Beyazit *et al. Angew. Chem., Int. Ed.***2016**, 55, 8244-8248.
3. M. Bompart, L. A. Gheber, Y. De Wilde, K. Haupt *Biosens. Bioelectron.* **2009**, 25, 568.
4. C. J. Addison, A. G. Brolo *Langmuir,* **2006**, 22, 8696-8702.

Monday, November 6, 2017

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Sławomir Sęk and Jingyuan Chen
09:00-09:40	T08	**Sergey Shleev** Biosupercapacitors
09:40-10:00	K17	**Patrizia R. Mussini** Strategies for High Enantioselectivity at Electrode Surfaces: Implementing Inherent Chirality in Electroactive Thin Films or Electrode|(Ionic Liquid) Interfaces
10:00-10:15	SC13	**Sebastian Mackowski** Wide-Field Fluorescence Microscopy of Real-time Conjugation Sensing
10:15-10:30	SC14	**Michal Kizling** Size Dependence of Gold Clusters Roles in Processes Catalyzed by Redox Enzymes
10:30-11:00		**Coffee break**
11:00-12:50		**Morning session 2** Chairs: Sergey Shleev and Patrizia R. Mussini
11:00-11:40	T09	**Krzysztof Winkler** Formation, Characterization, and Application of 1-D Polypyrrole Structures
11:40-12:00	K18	**Mathieu Etienne** Electroactive Artificial Biofilms
12:00-12:20	K19	**Klaus Mathwig** Fluorescent and Electrochemical Sensing Confined in Nanofluidic Channels
12:20-12:35	SC15	**Maciej Cieplak** Self-reporting Molecularly Imprinted Polymer for Label-free Selective Electrochemical Sensing of *p*-Synephrine
12:35-12:50	SC16	**Roberto Ortiz** Direct Electrochemistry of Cellobiose Dehydrogenases onto Gold Nanoparticle Modified Gold Electrodes-The role of surface charges
13:00-14:30		**Lunch**
14:30-16:25		**Afternoon session 1** Chairs: Krzysztof Winkler and Sebastian Mackowski
14:30-15:10	T10	**Francis D’Souza** Artificial Photosynthesis: Surface Modified Biomimetic Materials for Light Capture, Charge Separation, and Fuel Production

15:10-15:30	K20	**Wojciech Nogala** Nanoelectrodes for Determination of Silver Species in Biological Cells
15:30-15:50	K21	**Ilaria Palchetti** Nanostructured Electrochemical Platforms for the Detection of Clinically Relevant Molecules
15:50-16:10	K22	**Munetaka Oyama** Electrochemical Characteristics of Palladium Nano- or Micro-particles Modified Electrodes
16:10-16:25	SC17	**Magdalena Michalak** Micropattering of Bare Metallic Nanostructures and their Electrocatalytic Studies in Alkaline Media. SECM pH mapping
16:25-17:00		**Coffee break**
17:00-19:10		**Afternoon session 2** Chairs: Francis D’Souza and Wojciech Nogala
17:00-17:40	T11	**Gary Blanchard** Using Ionic Liquids to Control Interface Properties over Macroscopic Distances
17:40-18:00	K23	**Camelia Bala** Versatility and Challenges in the Design of Biosensors for Food Security
18:00-18:20	K24	**Vladimir Mirsky** Detection of Nano- and Microparticles of Engineered and Biological Origin by Wide-field Surface Plasmon Microscopy
18:20-18:35	SC18	**Marcin Holdynski** Collisions of Suspended Prussian Blue Nanoparticles with Rotating Disk Electrode
18:35-18:50	SC19	**Michael Füeg** Towards Mechanistic Understanding of Silver Nanoparticle Formation Catalyzed by *Geobacter sulfurreducens*
19:00-20:00		**Dinner**
21:00-		**Disco**

T08. Biosupercapacitors

Sergey Shleev

Department of Biomedical Science, Faculty of Health and Society,
Malmö University, Skåne, 20506 Malmö, Sweden
Kurchatov NBICS Centre, National Research Centre "Kurchatov Institute", 123182 Moscow, Russia
sergey.shleev@mah.se

The lecture will overview recent progress in the development of biosupercapacitors – supercapacitors fabricated using biological materials. In conventional biosupercapacitors the biomaterial serves as the pseudocapacitive component,[1,2] while in self-charging biodevices the biocomponent also functions as the biocatalyst.[3,4] The performance characteristics of biosupercapacitors are summarised and characterised in the perspective of the broader family of electric power devices,[5] including biodevices.[6] Self-charging biosupercapacitors show great promise in pulse-power delivery at the milliwatt level, typically greatly exceeding the capability of free-running bio-fuel and bio-solar cells.[7] Thus, chemical biosupercapacitors might be suitable for powering a new generation of miniaturized electronic applications,[8-13] including those intended for use in medical technology, while solar biodevices might be used as highly functional, but at the same time low-cost, environmentally friendly, and technically undemanding electric power sources.[14,15]

Acknowledgements
The author thanks the Swedish Research Council (project 2013-6006) for the financial support.

References

1. N. Malvankar, T. Mester, M. Tuominen, D. Lovley *ChemPhysChem* **2012**, *13*, 463.
2. E. González-Arribas, M. Falk, O. Aleksejeva, S. Bushnev, P. Sebastián, J. Feliu, S. Shleev *Electrochem. Commun.* **2017**, *in press*.
3. D. Pankratov, Z. Blum, D. Suyatin, V. Popov, S. Shleev *ChemElectroChem* **2014**, *2*, 343.
4. C. Agnès, M. Holzinger, A. Le Goff, B. Reuillard, K. Elouarzaki, S. Tingryb, S. Cosnier *Energy Environ. Sci.* **2014**, *7*, 1884.
5. D. Pankratov, P. Falkman, Z. Blum, S. Shleev *Energy Environ. Sci.* **2014**, *7*, 989.
6. D. Pankratov, Z. Blum, S. Shleev *ChemElectroChem* **2014**, *1*, 1798.
7. S. Shleev, E. González-Arribas, M. Falk *Curr. Opinion Electrochem.* **2017**, *in press*.
8. M. Kizling, S. Draminska, K. Stolarczyk, P. Tammela, Z. Wang, L. Nyholm, R. Bilewicz *Bioelectrochemistry* **2015**, *106*, 34.
9. D. Pankratov, F. Conzuelo, P. Pinyou, S. Alsaoub, W. Schuhmann, S. Shleev *Angew. Chem. Int. Ed.* **2016**, *55*, 15434.
10. M. Houghton, C. Santoro, F. Soavi, A. Serov, I. Ieropoulos, C. Arbizzani, P. Atanassov *Bioresour Technol.* **2016**, *218*, 552.
11. C. Narvaez Villarrubia, F. Soavi, C. Santoro, C. Arbizzani, A. Serov, S. Rojas-Carbonell, G. Gupta, P. Atanassov *Biosens. Bioelectron.* **2016**, *86*, 459.
12. X. Xiao, P. Conghail, D. Leech, R. Ludwig, E. Magner *Biosens. Bioelectron.* **2017**, *90*, 96.
13. S. Alsaoub, A. Ruff, F. Conzuelo, E. Ventosa, R. Ludwig, S. Shleev, W. Schuhmann *ChemPlusChem* **2017**, *82*, 576.
14. E. Gonzalez-Arribas, O. Aleksejeva, T. Bobrowski, M. Toscano, L. Gorton, W. Schuhmann, S. Shleev *Electrochem. Commun.* **2017**, *74*, 9.
15. G. Pankratova, D. Pankratov, K. Hasan, H.-E. Aakerlund, P.-A. Albertsson, D. Leech, S. Shleev, L. Gorton *Adv. Energy Mater.* **2017**, *7*, doi:10.1002/aenm.201602285.

K17. Strategies for High Enantioselectivity at Electrode Surfaces: Implementing Inherent Chirality in Electroactive Thin Films or Electrode|(Ionic Liquid) Interfaces

Serena Arnaboldi,[a] Giulio Apolloni,[b] Tiziana Benincori,[b] Silvia Cauteruccio,[a]
Emanuela Licandro,[a] Mariangela Longhi,[a] Mirko Magni,[a] Rocco Martinazzo,[a]
Simona Rizzo,[c] Francesco Sannicolò,[a] Patrizia R. Mussini[a]

[a] *Università degli Studi di Milano, Dipartimento di Chimica, Milano, Italy*
[b] *Università degli Studi dell'Insubria, Dipartimento di Scienza e Alta Tecnologia, Como, Italy*
[c] *Istituto di Scienze e Tecnologie Molecolari, CNR, Milano, Italy*
patrizia.mussini@unimi.it

Chiral electroanalysis could be regarded as the highest recognition degree in electrochemical sensing, implying the ability to discriminate between specular images of a given electroactive molecule in terms of significant peak potential difference. Since enantiomers have identical physico-chemical properties, the electron transfer process must take place in asymmetric conditions, exploiting a suitable chiral selector, such as a chiral electrode or a chiral medium. A groundbreaking strategy was recently proposed, based on the use of *inherently chiral* molecular selectors, either electrode surfaces[1] or media[2]. Inherent chirality implies the chirality source of the chiral selector to be neither localized nor external, but intrinsic to the whole main molecular backbone, featuring a tailored torsion; this can result in outstanding chirality manifestations. Thus, large differences in peak potentials have been observed for the enantiomers of different chiral probes: (a) working on inherently chiral electrode surfaces consisting of thin electroactive oligomer films[1] (often including macrocycle terms) electrodeposited from enantiopure inherently chiral monomers of different architectures, with either dissymmetric elements (dibenzothiophene, bithiophene or biindole atropoisomeric cores), or asymmetric elements (helicenes); (b) working on achiral electrodes, implementing inherent chirality in their interphase with an ionic liquid medium,[2] exploiting the latter's peculiarly high order. To this aim we developed inherently chiral ionic liquids ICILs as double salts of an atropoisomeric 3,3′-bipyridine scaffold with long alkyl chains and a suitable anion, resulting in melting points below room temperature. However, we found it even more convenient to employ the new ICILs as well as other family terms solid at room temperature as low-concentration chiral additives in commercial achiral ionic liquids: impressive peak potential differences, regularly increasing with additive concentration, have been observed for the enantiomers of different probes on achiral electrodes. Comparable results have also been obtained with other inherently chiral additives (bibenzimidazolium double salts and a helicene derivative). Work is in progress along both of the above lines, to strengthen and rationalize the first proofs of concepts by developing, characterizing and testing a wider variety of inherently chiral selectors (both surfaces and ionic liquids/additives), with different chiral probes, particularly of pharmaceutical interest, with more optimized and detailed protocols, and with the support of theoretical computations, particularly aiming to the recognition mechanism elucidation.

Acknowledgements

The inherent chirality research is currently supported by Regione Lombardia and Fondazione Cariplo (*Avviso congiunto per l'incremento dell'attrattività del sistema di ricerca lombardo e della competitività dei ricercatori candidati su strumenti ERC-edizione 2016*, Project 2016-0923).

References

1. *Angew. Chem. Int. Ed.*, **2014**, *53*, 2623-2627; *Chem. Eur J.* **2014**, *20*, 15298-15302; *Chem. Sci.* **2015**, *6*, 1706-1711; *Anal. Bional. Chem*. **2016**, 408, 7243-7254; *Chem. Eur J.* **2016**, *22*, 10839-10847; *New J. Chem.* **2017** DOI: 10.1039/C7NJ01501A; further works to be submitted.
2. *Angew. Chem. Int. Ed.*, **2017**, *56*, 2079-2082; further works to be submitted.

SC13. Wide-Field Fluorescence Microscopy of Real-time Conjugation Sensing

Marcin Szalkowski,[a] Ewa Roźniecka,[b] Justyna Grzelak,[a,c] Karolina Sulowska,[a] Dorota Kowalska,[a]
Joanna Niedziółka-Jönsson,[b] Sebastian Maćkowski,[a,c]

[a] *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University,*
Grudziadzka 5, 87-100 Torun, Poland
[b] *Institute of Physical Chemistry Polish Academy of Sciences,*
Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] *Baltic Institute of Technology, Al. Zwycięstwa 96/98, Gdynia, Poland*
mackowski@fizyka.umk.pl

We apply wide-field fluorescence microscopy to measure real-time attachment of photosynthetic proteins to plasmonically active silver nanowires. The observation of this effect is enabled on one hand by sensitive detection of fluorescence and, on the other hand, by plasmonic enhancement of protein fluorescence. We examined two sample configurations with substrates being a bare glass coverslip and a coverslip functionalized with a monolayer of streptavidin. The different preparation of the substrate changes the observed behavior as far as attachment of the protein is concerned and its subsequent photobleaching. For the latter, the conjugation process is measurably slower. The described method can be universally applied for studying protein-nanostructure interactions as they are taking place in real time.

Acknowledgements
Research was partially financed by the National Science Centre (Poland) within projects 2016/21/B/ST3/02276 and DEC-2013/10/E/ST3/00034, and the project 3/DOT/2016 funded by the City of Gdynia, Poland.

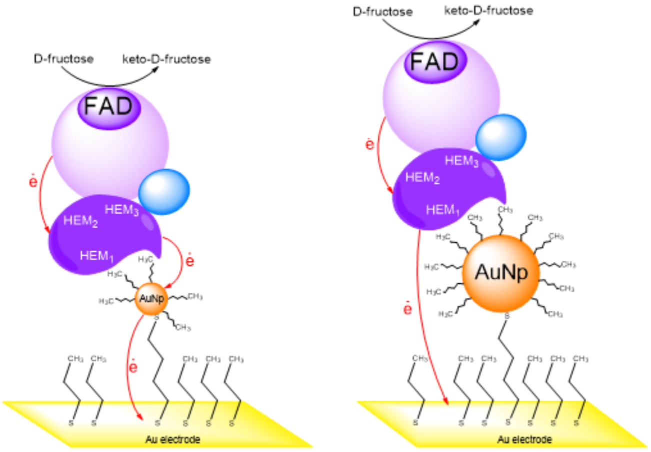
SC14.

Size Dependence of Gold Clusters Roles in Processes Catalyzed by Redox Enzymes

Michal Kizling, Maciej Dzwonek,[a] Agnieszka Wieckowska,[a] Renata Bilewicz[a]

[a] *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093, Warsaw, Poland*
[b] *College of Inter Faculty Individual Studies in Mathematics and Natural Sciences,*
University of Warsaw, Stefana Banacha 2C, 02 – 097, Warsaw, Poland
mkizling@gmail.com

Metal nanostructures are often utilized in bioelectrochemical systems for increasing electroactive surface area or conductivity[1]. We present here for the first time, both: thermodynamic and kinetic proofs that gold clusters are able not only to enhance the direct electron transfer (DET) but under special conditions they can also mediate ET between enzyme molecules and the electrode surface[2,3]. The role of these gold nanoparticles (NPs) depends on their size. NPs with core diameter lower than 2 nm were electrochemically active in aqueous media. Fructose dehydrogenase was used as the redox enzyme catalyzing oxidation of fructose. It was adsorbed on a self-assembled layer of gold clusters, 1-3.5 nm in diameter, hence smaller or similar to the size of the enzyme molecules. They were shown to enable fructose oxidation process at overpotentials reduced by at least 100 mV compared to those taking place on other nanostructured electrodes. Catalytic current density values divided by surface concentration of NPs were also larger indicating MET type of mechanism in case of the smallest NPs. This NP size-controlled switch of electron transfer from direct to mediated was confirmed by the increased electron transfer rate constants obtained from the rotating disc experiments at electrodes decorated with the smallest NPs.



References

1. D. Pankratov, R. Sundberg, D.B. Suyatin, J. Sotres, A. Barrantes, T. Ruzgas, I. Maximov, L. Montelius, S. Shleev *RSC Adv.* **2014**, *72*, 38164.
2. J.T. Holland, C. Lau, S. Brozik, P. Atanassov, S. Banta *J. Am. Chem. Soc.* **2011**, *133*, 19262.
3. J.M. Abad, M. Gass, A. Bleloch, D.J. Schiffrin *J. Am. Chem. Soc.* **2009**, *131*, 10229.

T09.

Formation, Characterization, and Application of 1-D Polypyrrole Structures

Krzysztof Winkler, Monika Wysocka-Zolopa, Izabela Zablocka

Institute of Chemistry, University of Bialystok, Ciolkowskiego 1K, 15-245 Bialystok, Poland
winkler@uwb.edu.pl

1-D polypyrrole structures were prepared by hard- and soft-template method. In the hard-template procedure, the mesoporous silica MCM-48 and MCM-41 were used. The silica mesopores were impregnated with dichloromethane solution of pyrrole by the capillary effect, and then monomer was polymerized in silica pores to form composite of polypyrrole and mesoporous silica. The polymer was deposited on the walls of mesopores. Therefore mesoporous structure was preserved in the composite. The polymer can be extracted from composite by silica dissolution in form of long wires.

In the soft template procedure, the 1-D conical structures of polypyrrole were formed in aqueous solution containing anionic and polymeric surfactants under electrochemical conditions. The process of conical structures deposition was initiated by formation of 'prenucleation' film of polypyrrole in solution containing perchlorate or tetrafluoroborate anions. The morphology, size, and aspect ratio of conical structures depend on the experimental conditions, such as: concentration of monomer, surfactant and supporting electrolyte, potential and time of electropolymerization.

The electrochemical properties of synthesized 1-D polypyrrole structures were investigated. All materials exhibit reversible charging/discharging properties and good electrochemical stability upon potential cycling. Due to the large real surface area they also show excellent capacitance properties. For example, the largest capacitance of approximately 400 Fg^{-1} was obtained for layer of conical polypyrrole structures. The polypyrrole wires and conical structures were also used for analytical determination of dopamine. The dopamine electrochemical sensors based on composite of MCM-48 and polypyrrole exhibit good selectivity, stability and low analyte detection level.

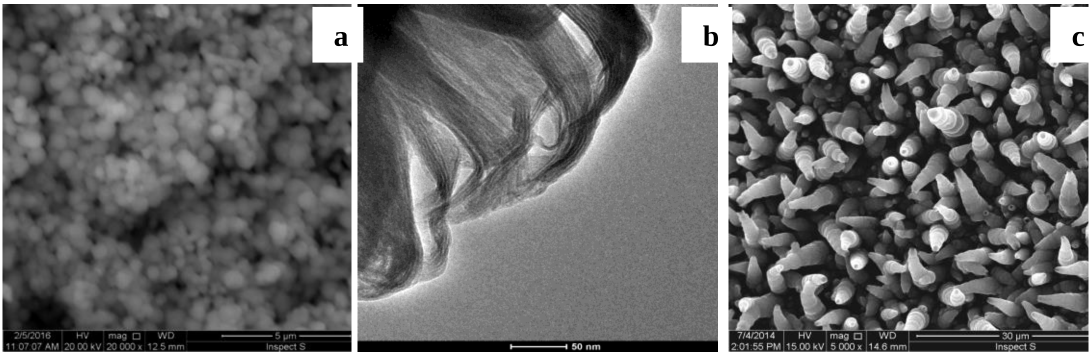


Figure 1. (a) SEM image of polypyrrole@MCM-48 composite, (b) TEM image of polypyrrole whiskers, and (c) SEM image of polypyrrole conical structures.

K18. Electroactive Artificial Biofilms

Mathieu Etienne

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

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

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

We have investigated the design of biocomposite materials comprising *Shewanella oneidensis, Geobacter sulfurreducens or Pseudomonas fluorescens*. The goal of this work was to promote biocomposite formation, bacterial viability and electron transfer reactions between electroactive bacteria, electron mediator and conductive materials. Different strategies have been evaluated in order to mimic natural biofilms, including loosely-bound cytochromes or nanowires.[1,2] Both anodic and cathodic reactions have been investigated. We will see that in biocomposites, it becomes critical to control the interface between individual bacteria and nanomaterials if one want to promote high viability or current, leading for example to a cathodic current density higher than 10 A m^{-2}. Tuning the interactions of bacteria with an electrode is also essential when considering imprinting approaches for analytical applications. These different biotechnological aspects will be discussed.

References

1. S. Pinck, M. Etienne, M. Dossot, F. P. A. Jorand *Bioelectrochemistry* **2017**, *118*, 131.
2. W. Ghach, M. Etienne, V. Urbanova, F. P. A. Jorand, A. Walcarius *Electrochem. Commun.* **2014**, *38*, 71.

K19. Fluorescent and Electrochemical Sensing Confined in Nanofluidic Channels

Klaus Mathwig

University of Groningen, Groningen Research Institute of Pharmacy, Pharmaceutical Analysis,
Antonius Deusinglaan 1, 9731 AV Groningen, The Netherlands
k.h.mathwig@rug.nl

The ability to sense smallest amounts of analyte molecules offers several advantages such as improved sensitivity and the possibility to handle smallest sample volumes, e.g., in point-of-care applications. When detection is performed at the single-molecule level, it allows studying complex reaction mechanisms, rare events, or subpopulations of complex biomolecules such as DNA or proteins whose individual properties are often hidden in ensemble measurements. Fluorescence microscopy is by far the most important tool for studying individual molecules, but it suffers from several drawbacks: reactions of molecules cannot be triggered easily during detection, high-throughput sensing is not possible, and often complex immobilization of target molecules on coverslip surfaces is required.

Here, we introduce a microfabricated nanofluidic flow cell to overcome these disadvantages. By confining the fluidic volume accessible by target molecules to an area that is smaller than the excitation/detection volume of a microscope objective, single molecules can be observed for prolonged times without the need for any immobilization. In addition, by introducing a nanochannel T-junction and driven flow, chemical reactions are continuously triggered in this junction and are observed at the single-molecule level as analytes are transported downstream the nanochannel. As proof of concept, we visualize enzymatically driven DNA synthesis in this nanofluidic flow cell.

Next to exclusively optical detection of fluorescence, the integration of electrodes into nanochannels allows the simultaneous electrochemical and optical sensing of molecules with combined electroactive and luminescent properties. We will demonstrate firsts result of electrochemiluminescence in the femtoliter confinement of a nanochannel.

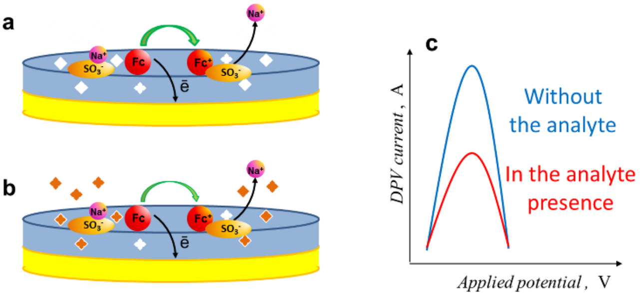
SC15.

Self-reporting Molecularly Imprinted Polymer for Label-free Selective Electrochemical Sensing. A Detailed Study of the "Gating Effect" in MIP Chemosensors

Patrycja Lach,[a] Maciej Cieplak,[a]* Piyush Sindhu Sharma,[a] Marta Sosnowska,[a] Krzysztof Noworyta,[a]
Francis D'Souza,[b]* and Wlodzimierz Kutner[a,c]*

[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, Woycickiego 1/3, 01-815 Warsaw, Poland

Molecularly imprinted polymers (MIPs) are excellent example of bio-mimicking recognition materials.[1] They have found numerous applications in selective chemosensing. For electrochemical determination of electroinactive analytes, usually some external redox probe is added to the sample solutions. It is assumed that binding of target analyte molecules by MIP molecular cavities causes MIP film swelling or shrinking. This behavior leads to changes in MIP film permittivity for the redox probe and thus changes in faradaic currents corresponding to reduction or oxidation of the redox probe (so called "gating effect") in CV and DPV determinations.[2] However, this mechanism seems to be inadequate for electrochemical sensors with conductive MIP film recognition units. For example, electrochemical impedance spectroscopy spectra recorded in our previous research[3] clearly indicate that redox probe diffusion to the electrode surface was not affected by analyte binding into MIP film. Moreover, well pronounced changes in charge transfer resistance were observed. These changes strongly suggest that drop of the redox probe oxidation peak in DPV determination originates from changes in electrochemical properties of the MIP film. Therefore, we can speculate that diffusion of a redox probe is a not crucial issue in terms of selective determination with the MIP film coated electrode. Therefore, a new specially designed monomer, vis., *p*-*bis*(2,2'-bithien-5-yl)methyl-ferrocene benzene was used for deposition of a self-reporting MIP film. This monomer acted as both a crosslinking monomer and an internal redox probe. It was electropolymerized together with 2,2'-bitiofen-5-carboxylic acid in the presence of the *p*-synephrine template – a diet supplement that is suspected of causing serious cardiovascular diseases. These self-reporting MIP film modified electrodes were used for electrochemical determination of *p*-synephrine in the absence of the external redox probe.



Scheme 1. Principle of operation of self-reporting MIP recognition layer based chemosensor in (a) absence and (b) presence of a target analyte, and (c) analytical DPV

References

1. M. Cieplak, W. Kutner *Trends Biotechnol.* **2016**, *34*, 922.
2. Y. Yoshimi, R. Yoshiizumi, R. Arai, I. Nakano, S. Sekine *J. Chem. Eng. Japan* **2009**, *42*, 600.
3. T. P. Huynh, C.B. KC, W. Lisowski, F. D'Souza, W. Kutner *Bioelectrochemistry* **2013**, *93*, 37.

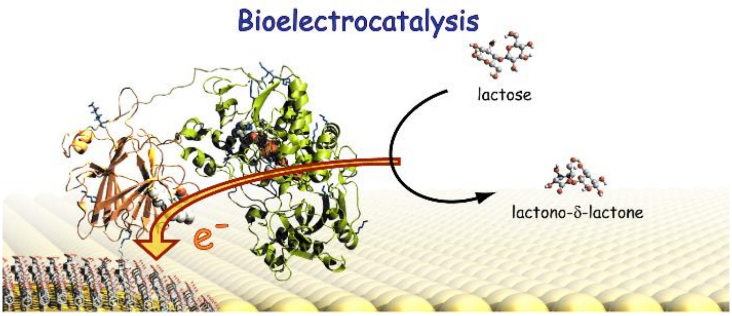
SC16.

Direct Electrochemistry of Cellobiose Dehydrogenases onto Gold Nanoparticle Modified Gold Electrodes – The Role of Surface Charges

R. Ortiz,[a,b] M. Tavahodi,[c] H. Matsumura,[d] R. Ludwig,[e] L. Gorton[b]

[a] *Dep. of Chemistry, Technical University of Denmark, Kgs. Lyngby, Denmark*
[b]*Dep. of Analytical Chemistry / Biochemistry and Structural Biology, Lund University, Lund, Sweden*
[c]*Dep. of Chemistry, Institute for Advanced Studies in Basic Sciences, Gava Zang, Zanjan, Iran*
[d]*Dep. of Biomaterials Sciences, Graduate School of Agriculture and Life Sciences,*
The University of Tokyo, Tokyo, Japan
[e]*Dep. of Food Sciences and Technology, BOKU University, Vienna, Austria*
Roberto.Ortiz@biochemistry.lu.se, Robor@kemi.dtu.dk

Cellobiose dehydrogenase (CDH) is an extracellular two domain redox enzyme, which is one of the very few redox enzymes that shows direct electron transfer (DET) properties with electrodes. The catalytically active dehydrogenase domain contains flavin adenine dinucleotide (FAD) and the other, the cytochrome domain, contains heme *b*. For the native enzyme only the heme domain shows DET properties reflected by that the redox conversion of the heme group is shown in a cyclic voltammogram.[1,2] CDH is able to oxidize important carbohydrates for the dairy industry and human health, as lactose and glucose. Achieving efficient electrochemical communication between redox enzymes and electrode materials is one of the main challenges in bioelectrochemistry and is of great importance for developing bioelectronic devices for real applications. In this work, it is presented firstly how the deposition of gold nanoparticles (AuNPs) onto solid Au electrodes were used to increase the surface-aspect-ratio and secondly how the introduction of charges on the AuNPs dramatically increases the electrocatalytic efficiency of CDH in the presence of substrate. The AuNPs were synthesized by citrate reduction and were post-modified using either charged polymers (polyethyleneimine or poly(sodium-4-styrenesulfonate)) or a mixture of thiols (4-aminothiophenol, 4-mercaptobenzoic acid, 4-mercaptophenol, 11-mercapto-1-undecanamine, 11-mercapto-1-undecanoic acid, and 11-mercapto-1-undecanol). Using this synthetic pathway, neutral, negatively and positively charged surfaces were obtained. The highest electrocatalytic efficiency of sugars of immobilized CDH onto such AuNP modified electrodes was found to be on positively charged surfaces. The heterogeneous electron-transfer (ET) rate (k_s) for the redox reaction of immobilized CDH was calculated based on the Laviron theory for the first time.[3,4] The work found the basis for lactose and glucose biosensors and bioanodes.[5]



References

1. R. Ludwig, R. Ortiz, C. Schulz, W. Harreither, C. Sygmund, L. Gorton *Anal. Bioanal. Chem.* **2013**, *405*, 3637.
2. P. Bollella, R. Ludwig, L. Gorton *Appl. Mater. Today*, **2017**, *9*, 319.
3. H. Matsumura, R. Ortiz, R. Ludwig, K. Igarashi, M. Samejima, L. Gorton *Langmuir* **2012**, *28*, 10925.
4. M. Tavahodi, R. Ortiz, C. Schulz, A. Ekhtiari, R. Ludwig, B. Haghighi, L. Gorton *ChemPlusChem*, **2017**, *82*, 546.
5. X. Wang, M. Falk, R. Ortiz, H. Matsumura, J. Bobacka, R. Ludwig, M. Bergelin, L. Gorton, S. Shleev *Biosens. Bioelectron.* **2012**, *31*, 219.

T10. Artificial Photosynthesis: Surface Modified Biomimetic Materials for Light Capture, Charge Separation, and Fuel Production

Gowri Mohandass, Youngwoo Jang, Mei-Li Kincaid, Christopher Obondi,
Shivaraj Yellappa, and Francis D'Souza

Department of Chemistry, University of North Texas,
1155 Union Circle, #305070, Denton, TX 76203-5017, USA
Francis.DSouza@unt.edu

To tackle the ever increasing energy demand of modern society and avoid environmental pollution caused by burning fossil fuels, solar energy is perhaps the most attractive, renewable, clean and inexhaustible energy source. Therefore, efficient capture and conversion of solar energy into chemical energy and electricity by utilizing molecular systems that follow the concept artificial photosynthesis has witnessed rapid growth during recent years. In the design, multi-modular donor-acceptor systems capable of wide-band light capture for maximum utilization of sun light, and subsequently perform the process of photoinduced electron transfer leading to long-lived charge separated states of sufficient stored energy are key factors. The stored energy in the electron transfer products will be subsequently utilized for light-to-electricity and light-to-fuel production. The talk will present recent developments in our laboratory on the research topic of building supramolecular systems capable of visible-near infrared light capture, and transporting the captured light to the donor-acceptor site for carrying out successive light induced electron transfer resulting in high potential charge separated states in solution and electrode surfaces. Further, utilization of surface modified artificial photosynthetic systems for solar fuel production will also be highlighted.

K20. Nanoelectrodes for Determination of Silver Species in Biological Cells

Wojciech Nogala, Magdalena Michalak, Aleksandra Szymańska,
Kinga Matuła, Małgorzata Kurel, Marcin Opałło

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland
wnogala@ichf.edu.pl

Antibacterial properties of silver nanoparticles (AgNPs) are utilized in a number of applications and consumer products, such as medicine, water and air purification, cosmetics and clothing. Their widespread use also becomes potentially harmful for the ecosystem. AgNPs have been shown to be effective agents against many strains of bacteria, fungi and viruses.[1] However, some infective entities exhibit high resistance to AgNPs treatment or are even able to synthesize AgNPs from Ag^+.[2] Clinical use of AgNPs as an antibiotic require their selective effectiveness against infection and safety for patients. This cannot be achieved without sufficient understanding of the antimicrobial action of AgNPs. There are a few propositions of contradictory hypothetical mechanisms presented in the literature reports, i.e. uptake of Ag^+ ions followed by disruption of ATP production and DNA replication,[3] release of silver ions followed by generation of reactive oxygen species,[5] or direct damage to cell membranes by AgNPs.[6]

Nanoelectrodes have been used for AgNPs detection by nanoimpact technique[7] and for studies of nucleation and growth of Ag clusters by electroreduction of Ag+.[8] Recent reports suggest, however, that applicability of nanoimpact coulometry for nanoparticle sizing is questionable.[9,10]

In this study we use carbon nanoelectrodes for extracellular and intracellular electroanalytical measurements in suspension of AgNPs or silver salt solution. We are focused on verification of applicability of nanoimpact coulometry for AgNPs sizing as well as elucidation of mechanism of antibacterial action of AgNPs. Nanoelectrodes are positioned inside selected eukaryotic cells, with the help of scanning electrochemical microscopy equipment and optical microscopy.

References

1. G. Franci, A. Falanga, S. Galdiero, L. Palomba, M. Rai, G. Morelli, M. Galdiero, *Molecules,* **2015**, *20*, 8856.
2. F. M. Morsy *Arch. Microbiol.* **2015**, *197*, 645.
3. P. V. AshaRani, G. L. K. Mun, M. P. Hande, S. Valiyaveettil *ACS Nano* **2009**, *3*, 279.
4. E. T. Hwang, J. H. Lee, Y. J. Chae, Y. S. Kim, B. C. Kim, B.I. Sang, M. B. Gu *Small* **2008**, *4*, 746.
5. H. J. Park, J. Y. Kim, J. Kim, J. H. Lee, J. S. Hahn, M. B. Gu, J. Yoon *Water Res.* **2009**, *43*, 1027.
6. A. B. Smetana, K. J. Klabunde, G. R. Marchin, C. M. Sorensen *Langmuir* **2008**, *24*, 7457.
7. J. Clausmeyer, P. Wilde, T. Löffler, E. Ventosa, K. Tschulik, W. Schuhmann *Electrochem. Commun.* **2016**, *73*, 67.
8. J. Velmurugan, J-M. Noel, W. Nogala, M. V. Mirkin *Chem. Sci.* **2012**, *3*, 3307.
9. S. M. Oja, D. A. Robinson, N.J. Vitti, M. A. Edwards, Y. Liu, H. S. White, B. Zhang *J. Am. Chem. Soc.*, **2017**, *139*, 708.
10. J. Ustarroz, M. Kang, E. Bullions, P. R. Unwin *Chem. Sci.* **2017**, *8*, 1841.

K21.

Nanostructured Electrochemical Platforms for the Detection of Clinically Relevant Molecules

Francesca Bettazzi, Ilaria Palchetti

Department of Chemistry, University of Florence, Italy
ilaria.palchetti@unifi.it

Electrochemical techniques, such as faradic impedance spectroscopy, amperometry, and differential pulse voltammetry, have been used by our group, for the development and characterization of different formats of genosensors. Basically, the DNA capture probes are immobilized on the electrode surfaces. Then, the target sequence is extracted from the sample, and hybridized with the specific capture probes. Different label and label-free detection methods have been optimized [1,2].

However, it is well known that the electrode surface nanostructuring offers suitable anchoring sites for the capture probes allowing optimal control over steric hindrance, increased surface area and increased mass transport rate. Thus, recently, we have investigated different nanostructured electrochemical platforms for the sensitive detection of nucleic acids. In a first attempt, a procedure to electrochemically deposit Au nanoclusters, in order to define nanoscale immobilization Au domains over a carbon electrode surface, was optimized [3]. Then, a label-free impedimetric genosensor, using a functional polymer-modified sensor was developed [4]. Finally, colloidal nanoparticle-modified graphene-based electrochemical platforms have been studied. The main advantages of graphene-based electrodes are a large potential window, fast heterogeneous electron transfer kinetics for various analytes and the involvement of additional "chemical features" (e.g. aromatic structures strongly connecting graphene via π−π stacking interactions). Graphene oxide (GO) is a highly oxidized form of graphene consisting of single atom-thick layers of graphene sheets with carboxylic acid, epoxide and hydroxyl groups in the plane. GO can be obtained in bulk quantities through extensive oxidation/exfoliation of graphite. The reduced form of graphene oxide (rGO) can provide GO with enhanced and modified optical and electrical properties. GO and rGO are emerging materials for biosensing applications. The integration of Au nanoparticles (NPs) into GO or rGO nanoflakes allows in certain cases to an efficient improvement of the device sensitivity due to enhancement of the electron transfer or through its surface catalytic reaction with certain analytes. The behavior of a novel AuNPs-rGO nanostructure was, herein, investigated towards electrochemical sensing of clinically relevant molecules and towards the development of a DNA-based biosensor.

References

1. I. Palchetti, S. Laschi, G. Marrazza, M. Mascini *Anal. Chem.* **2007,** *79*, 7206.
2. F. Bettazzi, F. Lucarelli, I. Palchetti, F. Berti, G. Marrazza, M. Mascini *Anal. Chim. Acta* **2008**, *614*, 93.
3. D. Voccia, F. Bettazzi, E. Fratini, D. Berti, I. Palchetti *Anal. Bioanal. Chem.* **2016,** *408*, 7271.
4. D. Voccia, M. Sosnowska, F. Bettazzi *et al. Biosens. Bioelectron.* **2017**, *87*, 1012.

K22.

Electrochemical Characteristics of Palladium Nano- or Micro-particles Modified Electrodes

Munetaka Oyama

Department of Materials Chemistry, Graduate School of Engineering
Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan
oyama.munetaka.4m@kyoto-u.ac.jp

Palladium nanoparticles (PdNPs) modified conducting substrates have been attracting active attention due to their effectiveness in catalysis, electrocatalysis, hydrogen storage, etc. More than 10 years ago, we reported that PdNPs were successfully grown on the indium tin oxide (ITO) surface by using the seed mediated growth method.[1] Actually, PdNPs could be modified on ITO through two steps immersions, i.e., the first in a seed solution for attaching Pd nano-seeds and the second in a growth for nanoparticles growth. By using this approach, unique PdNPs/ITO surfaces could be prepared and their electrochemical characteristics were reported.[1]

Recent years, we are interested in the galvanic replacement preparations for preparing nano- or micro-structures of noble metals on base metals. In the case of Pd, the combination with Ni was found to be effective to prepare Pd nano- or micro-crystals on the base Ni electrode. So, in the first part of this presentation, the galvanic replacement preparation of Pd modified Ni will be presented together with the electrochemical characteristics. Also, the combinations with other base metals are presented with their electrocatalytic properties.

On the other hand, we reported the modification of AuNPs on a Pd base electrode showed an unusual oxidation wave in an alkaline aqueous solution.[2] This phenomenon could be attributed to the interfacial catalytic oxidation of water.[2] However, in the experiments, the reproducibility is not good, and, in the construction of the AuNPs/Pd electrodes, careful polish of the base Pd was essential to obtain the catalytic oxidation wave. Therefore, to utilize this phenomenon e.g. in fuel cells, we would like to extend the study for combining AuNPs with Pd micro-particles instead of a Pd disk electrode. However, as the actual results, in the preliminary trials using some Pd micro-particles without AuNPs, we have fond that the electrochemical responses of Pd micro-particles strongly depends on the crystal shapes.

Concerning the above results, various electrochemical characteristics of Pd nano- or micro-particles modified electrodes will be presented and discussed in the workshop.

References

1. G. Chang, M. Oyama, K. Hirao *J. Phys. Chem. B* **2006**, *106*, 20362.
2. Y. Nakayama, M. Oyama *Chem. Commun.* **2013**, *49*, 5228.

SC17.

Micropattering of Bare Metallic Nanostructures and their Electrocatalytic Studies in Alkaline Media. SECM pH mapping

Magdalena Michalak, Wojciech Nogala, Martin Jönsson-Niedziolka, Marcin Opallo

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

The main objective of this study is to obtain bare, metallic nanostructures using Scanning Electrochemical Microscopy (SECM), and to examine their electrocatalytic properties, using selected electrode processes involving hydrogen cations and hydroxyl anions reagents. Micrometer-sized samples of copper and gold nanostructures were obtained on transparent tin-doped indium oxide (ITO) and glassy-carbon (GC) electrodes with sacrificial microelectrodes made of polycrystalline metals.[1] Electrocatalytic reactions which were studied occur on the obtained nanostructures. The first – oxygen reduction reaction (ORR)[2] in alkaline media is important in the conversion of the chemical energy to electricity. The second – carbon dioxide reduction reaction (CO_2RR)[3] suggests a new approach to saving of fossil fuels, energy storage and reduction of carbon dioxide in the atmosphere. When protons or hydroxyl anions act as reagents of the process (like in the reactions described above), the pH reaction of the solution is different near the surface of the catalyst than in the bulk solution. It may has an influence on the mechanism of the undergoing reaction and on the structure of catalysts. The aim of this study is to detect these local and subtle changes of the pH near the surface of obtained nanostructures and to see where these changes occur. It can be achieved by using pH nanosensor[4] which can be used to record the map of the pH changes during reaction and, at the same time, to allow to record a nanoscale map of the topography of the sample.

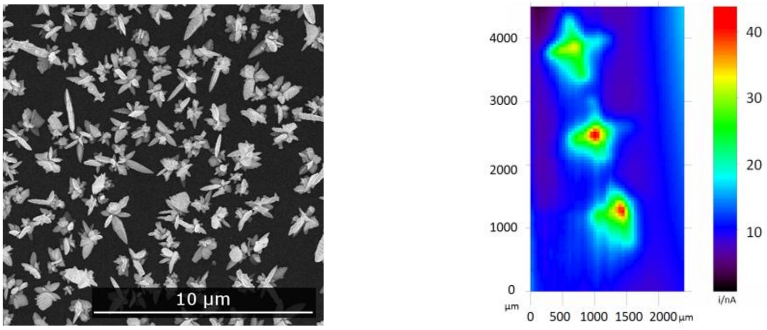


Figure 1. a) Copper nanostructures obtained at the ITO electrode in 10 mM HCl + 1 M KCl solution. b) SECM scan of feedback mode carbon dioxide reduction in 30mM HCOOH + 0.1 M phosphate buffer (pH = 7) solution over crossed copper and gold nanoparticles on the GC electrode.

References

1. W. Nogala, K. Palanisamy, S. Gawinkowski, M. Jönsson-Niedziolka, M. Kominiak, J. Waluk, M. Opallo *Nanoscale*, **2015**, *7*, 10767
2. I. Katsounaros, S. Cherevko, A. R. Zeradjanin, K. J. J. Mayrhofer *Angew. Chem. Int. Ed*. **2014**, 53, 102.
3. J. Monzó, Y. Malewski, R. Kortlever, F. J. Vidal-Iglesias, J. Solla-Gullón, M. T. M. Koperand, P. Rodriguez *J. Mater. Chem. A* **2015**, *3*, 23690
4. M. Michalak, M. Kurel, J. Jedraszko, D. Toczydlowska, G. Wittstock, M. Opallo, W. Nogala *Anal. Chem*. **2015**, *87*, 11641

T11. Using Ionic Liquids to Control Interface Properties over Macroscopic Distances

Ke Ma and G. J. Blanchard

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

We have found that it is possible to induce long range order (*ca*. 100 μm) in room temperature ionic liquids (IL) by means of applying a potential to the surface on which the IL resides. We have used 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF4^-$), supported on a silica surface to demonstrate the effect. Long-range ordering, over five orders of magnitude greater than predicted by the Guoy-Chapman or similar models, can be seen in the rotational diffusion dynamics three structurally similar dyes, where one is anionic, one is cationic and a third is neutral. The rotational diffusion time constants of the charged dyes vary in a regular manner as a function of distance from the (charged) support surface. We model these data in the context of an excess charge density gradient being induced in the IL by the charge present on the support. The effect depends directly on the surface charge and affords a novel means of establishing the potential of zero charge (pzc) for the support material. Rotational diffusion measurements of these same chromophores in ethylene glycol are spatially invariant, demonstrating that this effect is associated with the ionic liquid. Capping the silica support with Me_2SiCl_2 prevents the establishment of a charge density gradient also, demonstrating the need for surface charge to induce long-range order in ILs. The IL exhibits a spatially-damped piezoelectric response mediated by IL fluidity and disorder, and we consider the potential of this effect for controlling interface properties.

K23.

Versatility and Challenges in the Design of Biosensors for Food Security

Camelia Bala

University of Bucharest, Department of Analytical Chemistry,
4-12 Regina Elisabeta Blvd., Bucharest, Romania
camelia.bala@chimie.unibuc.ro

Biosensor technology represents an extremely wide field with an increased interest for application in food and agriculture industries. Enzyme-based biosensors can be used in food quality control to measure amino acids, amides, amines, carbohydrates, heterocyclic compounds, carboxylic acids, gases, inorganic ions, coenzymes, alcohols and phenols. Carbohydrates, alcohols, and acids are usually monitored in the control of the fermentation processes for producing wine, beer or yoghurt. The inhibition-based biosensors are used as alarm systems for detecting a class of compounds such as pesticides, mycotoxins or biogenic amines. These platforms are suitable for fast screening of the food samples for toxic compounds or in the freshness tests.

One of the most important step in preparing the biosensors is the immobilization of the bio-component on the surface of the transducer. Physical adsorption, entrapment in a porous matrix (polymers, polyelectrolytes, hydro-gels), layer by layer technique or chemical immobilization represents the main immobilization methods reported in the literature. Advantages and limitations of these techniques will be presented in this lecture[1-4].

Real progresses were made in improving of the biosensor performances such as detection limit, sensitivity and selectivity by using an appropriate design of the interface. Innovation in materials science, nanotechnology and biomimetic design are reinforcing the biosensor field. A significant amount of research has gone on the use of nanomaterials in the preparation of the biosensors to improve the analytical features. Detection limits at the level of nM to fM were achieved, which, in general, are below the maximum accepted level by the European legislation in food products.

The integration of the biosensors in simple, cheap and portable system represents a challenge for commercially available biosensors or for the phase of biosensors implementation for release on the market. Multi-analyte detection on multiplexed systems, development of sensor networks and wireless signal transmitters for remote sensing will definitively mark the future of the biosensors for food quality control.

References

1. L. Rotariu, F. Lagarde, N. Jaffrezic-Renault, C. Bala *TrAC, Trends Anal. Chem.* **2016**, *79*, 80.
2. L.G. Zamfir, I. Geana, S. Bourigua, L. Rotariu, C. Bala *Sens. Actuators, B* **2011,** *159*, 178.
3. M. Puiu, O. Istrate, L. Rotariu, C. Bala, *Anal. Biochem.* **2012**, *421*, 587.
4. M. Puiu, A.-M. Gurban, L. Rotariu, S. Brajnicov, C. Viespe, C. Bala, *Sensors,* **2015**, *15*, 10511.

K24. Detection of Nano- and Microparticles of Engineered and Biological Origin by Wide-field Surface Plasmon Microscopy

Vladimir M. Mirsky

Brandenburg University of Technology Cottbus-Senftenberg, Germany
mirsky@b-tu.de

Detection and analysis of nano- and microparticles of different origin is an important task for chemical analytics, medical diagnostics, food industry, biotechnology, environmental monitoring and for many other fields of science and industry. For this purpose, a method based on the detection and analysis of minute signals of surface plasmon resonance images due to adsorption of single particles was developed.

The new technology allows one a real-time detection of interaction of single nanoparticles of different origin with the sensor surface. Adsorption of each nanoparticle leads to a characteristic diffraction image whose intensity depends on the size and chemical composition of the particle. A number of the nanoparticle–surface binding events per time and surface area characterizes volume concentration. A large monitored surface area of the sensor surface allows one to detect many hundreds of events in each frame or totally up to a million particles on the sensor surface; this leads to a very high dynamic range of counting and to a correspondingly high dynamic range in the concentration scale. Depending on the type of particles and experimental conditions, the detection limit for aqueous samples can be below 100 nanoparticles per microliter. Stable analysis of nanoparticles in very complex environments (fruit juice, cosmetic formulations) was demonstrated.

To determine chemical composition of single nanoparticles separately, the wide field surface plasmon microscopy can be used as a tandem technique. For example, to analyze technical nanoparticles, it can be assisted by electrochemical system. In this case, the gold sensor surface is used both for plasmon microscopy and as the working electrode of the electrochemical cell. Applying a linear potential sweep to this electrode, adsorbed nanoparticles can be subjected to electrochemical conversion, leading to the change of their refractive index; the value of electrical potential of this conversion characterizes the material of the particular nanoparticle. Notably, such analysis is performed simultaneously but independently for each adsorbed particle.

The method of wide field surface plasmon microscopy can be applied for ultrasensitive detection and analysis of nano- and microparticles of biological (bacteria, viruses, endosomes), biotechnological, (liposomes, protein nanoparticles for drug delivery) or technical (metallic, oxides, plastic, etc.) origin.

References

1. S. Nizamov, O. Kasian, V. M. Mirsky *Angew. Chem. Int. Ed.* **2016**, *55*, 7247.
2. S. Nizamov, V. Scherbahn, V. M. Mirsky *Anal. Chem.* **2016**, *88*, 10206.
3. I. Sidorenko, S. Nizamov, R. Hergenröder, A. Zybin, A. Kuzmichev, B. Kiwull, R. Niessner, V. M. Mirsky *Microchim. Acta*, **2016**, *183*, 101.
4. V. Scherbahn, S. Nizamov, V. M. Mirsky *Microchim. Acta*, **2016**, *183*, 2837.
5. Nizamov, S., Mirsky, V. M. *Detection, quantification and characterization of nanoparticles by means of surface plasmon microscopy*. In: Challa S. S. R. Kumar (eds.) *In-situ Characterization Techniques for Nanomaterials*, Springer, **2018**.

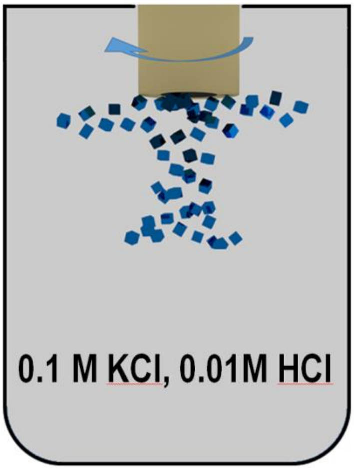
SC18. Collisions of Suspended Prussian Blue Nanoparticles with Rotating Disk Electrode

Marcin Holdynski, Joanna Dolinska and Marcin Opallo

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

The electrochemistry of suspended nanoparticles received recently some attention[1] because of the challenge in recording of single electrochemical events, evaluation of nanoparticles reactivity and determination of their size or concentration. Although the majority of experiments were done with microelectrodes in quiescent conditions, we have demonstrated that electrochemical response of catalytic nanoparticles can be detected in forced convection conditions.[2] Subsequent injections of gold nanoparticles suspension into glucose solution result in step like current-time characteristics obtained with rotating disc electrode (RDE). This is due to electrocatalytic oxidation of glucose at nanoparticles being the electric contact with inert electrode. Similarly, addition of carbon nanoparticles suspension into ascorbate solution flow results in appearance of peak on current-time shaped dependence obtained with inert electrode due to electrocatalytic oxidation of ascorbate.[3]

Here, we demonstrate that suspended redox active nanoparticles exhibit electrochemical reactivity under hydrodynamic conditions. This was done on the example of Prussian Blue nanoparticles (PBNPs), exhibiting well defined electrochemical redox processes. Conducted measurements demonstrated that subsequent injection of PBNPs results in subsequent current increases resulting from their electroreduction or electrooxidation. This indicates that suspended nanoparticles approach the electrode close enough to allow for electron transfer. Such a method of characterization may be useful not only from fundamental point of view but also in research oriented towards PBNPs application in electrochemical devices.



References

1. S.V. Sokolov, S. Eloul, E. Katelhon, C. Batchelor-McAuley and R.G. Compton *Phys. Chem. Chem. Phys.* **2017**, *19*, 28.
2. J. Dolinska, M. Jonsson-Niedziolka, V. Sashuk and M. Opallo *Electrochem. Commun.* **2013**, *37*, 100.
3. W. Cheng, X. -F. Zhou and R.G. Compton *Angew. Chem. Int. Ed*. **2013**, *125*, 13218.

SC19.

Towards Mechanistic Understanding of Silver Nanoparticle Formation Catalyzed by *Geobacter sulfurreducens*

Michael Füeg,[a] Katharina M. Fromm,[b] Bernd Giese[b]

[a]*Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland*
[b]*Department of Chemistry, University of Fribourg, Fribourg, Switzerland*
michael.fueeg@dcb.unibe.ch

The ability of the versatile microorganism *Geobacter sulfurreducens* (*Gs*) to transport its respiratory electrons to extracellular electron acceptors has many applications in emerging technologies[1]. Originally evolved as anaerobic strategy for mineral respiration, this process can be redirected to anodes in microbial fuel cells or used to biosynthesize metal nanoparticles from the corresponding metal cations.[2-4]

In microbial fuel cells, the anode surface can be modified by a biofilm of *Gs* that catalyzes the oxidation of acetate to CO_2 and wires the electrons to the anode for electricity production[5]. There, a high conductivity through the biofilm and the microbe-anode interface is crucial for efficient electricity production in applied wastewater cleaning devices. However, indications towards a limitation to the current production by electron transfer through the biofilm exists. The discovery of the silver nanoparticle formation by *Gs* from silver nitrate may provide an elegant way to incorporate silver nanoparticles into a *Gs* biofilm. Incorporated metal nanoparticles, in turn, may assist in the electron transfer through the biofilm. This additionally opens the possibility to precipitate silver nanoparticles from wastewater[6] as further cleaning strategy. To successfully implement this method in research, detailed understanding of the underlying mechanism of the microbe-mediated silver nanoparticle formation is needed.

Here, we present new insights into the mechanism of silver nanoparticle formation from silver ions using *Gs* as catalyst. We found additional[7–10] evidence for the involvement of cytochromes under anaerobic conditions by monitoring the UV/Vis absorbance of the Soret and Q bands of the heme units. This method allows to visualize the "breathing" of *Gs* during the synthesis of silver nanoparticles, which could access the rates of the extracellular electron transfer by tuning the concentration of the electron acceptor.

References

1. Lovley, D. R. *Annu. Rev. Microbiol.* **2012**, *66*, 391.
2. D. L. Cologgi, A. M. Speers, B. A.Bullard, S. D. Kelly, G. Reguera *Appl. Environ. Microbiol.* **2014**, *80*, 6638.
3. M. D. Yates, R. D. Cusick, B. E. Logan *ACS Sustain. Chem. Eng.* **2013**, *1*, 1165.
4. N. Law, S. Ansari, F. R. Livens, J. C. Renshaw, J. R. Lloyd *Appl. Environ. Microbiol.* **2008**, *74*, 7090.
5. D. R. Bond, D. R. Lovley *Appl. Environ. Microbiol.* **2003**, *69*, 1548.
6. O. Modin, F. Aulenta, F. Harnisch *et al*. *Environ. Sci. Water Res. Technol.* **2017**, *156*, 1.
7. M. Estevez-Canales, A. Kuzume, Z.Borjas *et al. Environ. Microbiol. Rep.* **2015**, *7*, 219.
8. F. Caccavo, D. J. Lonergan, D. R. Lovley *et al. J. Appl. Environ. Microbiol.* **1994**, *60*, 3752.
9. J. P. Busalmen, A. Berná, J. M. Feliu *Langmuir* **2007**, *23*, 6459.
10. D. Millo, F. Harnisch, S. A. Patil *et al. Angew. Chemie Int. Ed.* **2011**, *50*, 2625.

This page intentionally left blank

Tuesday, November 7

08:00-09:00		**Breakfast**
09:00-10:30		**Morning session 1** Chairs: Vladimir Mirsky and Gary Blanchard
09:00-09:40	T12	**Ambra Giannetti** Spatially-selected Optical Microbubble Resonators for Biomolecule Immobilization
09:40-10:00	K25	**Gabriela Almeida** Construction of Electrochemical Biosensors for Nitrite Detection: Needs, Challenges and Perspectives
10:00-10:15	SC20	**Jan Hrbac** Electrode Modification by Metal-derived Nanostructures using Interelectrode Material Transfer and Spark Discharges
10:15-10:30	SC21	**Bhavana Gupta** Wireless Actuation of Conducting Polymers
10:30-11:00		**Coffee break**
11:00-12:10		**Morning session 2** Chairs: Gabriela Almeida and Ilaria Palchetti
11:00-11:40	T13	**Lo Gorton** Electrochemical Communication Between Photosynthetic Membranes/Cells and Electrodes for Harvesting Solar Energy
11:40-12:00	K26	**Jingyuan Chen** High-response Conducting Films Made of Suspensions of Polyaniline-coated Graphene
12:00-12:10		Closing
12:10-13:10		**Lunch**
13:10-		**Departures**

T12. Spatially-selected Optical Microbubble Resonators for Biomolecule Immobilization

S. Berneschi,[a] F. Baldini,[a] A. Cosci,[a] D. Farnesi,[b,a] G. Nunzi Conti,[a,b]
S. Tombelli,[a] C. Trono,[a] S. Pelli,[a,b] A. Giannetti[a]

[a] *IFAC-CNR, Istituto di Fisica Applicata "Nello Carrara", Sesto Fiorentino (FI), Italy*
[b] *Centro "Enrico Fermi", Rome, Italy*
a.giannetti@ifac.cnr.it

In the optical sensing area, the integration between the microfluidics and the optical transducer represents one of the main requirements towards the development of a more and more miniaturized sensors with high performances in terms of sensitivity and limit of detection.[1] In particular, the advances in microtechnologies have recently led to a new class of sensing devices represented by the so-called optical microbubble resonators (OMBR), which well satisfy the aforementioned specifications thanks to their intrinsic characteristics. In fact, these hollow core microcavities can be effectively considered as a localized swelling induced in silica microcapillaries by a suitable fabrication process.[2,3]

The biosensing mechanism of these devices is based on the morphological dependence of the whispering gallery modes: any change on the OMBR inner surface, due to some chemical and/or biochemical binding, causes a shift of the resonance position and reduces the Q factor of the OMBR. By measuring these changes, important information about the sensing capability of the device can be obtained. In order to develop an OMBR-based biosensor and to optimize its performance, a crucial step is represented by the chemical/biochemical functionalization of its internal surface. Here we present a novel technique able to guarantee that the chemical interaction occurs in the OMBR inner wall, leaving the other microfluidic parts completely inert from a biochemical point of view. The method is based on UV photoactivation, which allows localizing the biolayers only in correspondence of the OMBR inner wall (Figure 1).[4]

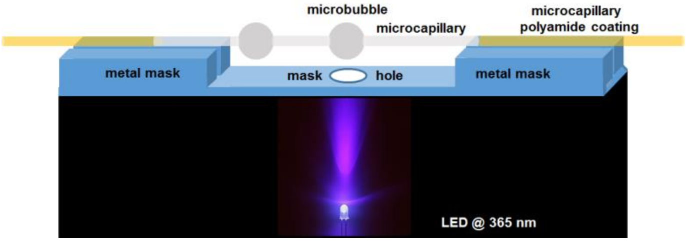


Figure 1. A sketch of the OMBR photo-activation by means of UV light focused onto the microbubble through a metal mask.

As a proof of concept, an immunoassay based on IgG/anti-IgG interaction was performed. The anti-IgG antibody was labelled with Alexafluor488 to verify, by a fluorescence characterization, the goodness of this procedure. The high Q factor (> 10^5) measured after the IgG/anti-IgG interaction in water gives a further proof for the method validity.

References

1. H. Zhu, I.M. White, J.D. Suter, M. Zourob, X. Fan *Analyst*, **2008**, *132*, 356.
2. M. Sumetsky, Y. Dulashko, R. S. Windeler *Opt. Lett.*, **2010**, *35*, 898.
3. S. Berneschi, D. Farnesi, F. Cosi, G. Nunzi Conti, S. Pelli, G. Righini, S. Soria *Opt. Lett.* **2011**, *36*, 3521.
4. S. Berneschi, F. Baldini, A. Cosci, D. Farnesi, G. Nunzi Conti, S. Tombelli, C. Trono, S. Pelli, A. Giannetti *Sens. Actuators B* **2017**, *242*, 1057.

K25.

Construction of Electrochemical Biosensors for Nitrite Detection: Needs, Challenges and Perspectives

M. Gabriela Almeida[a,b]

[a]UCIBIO, REQUIMTE, Faculdade de Ciências e Tecnologia,
Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
[b]CiiEM, Inst. Superior de Ciências da Saúde Egas Moniz, 2829-511 Caparica, Portugal
mg.almeida@fct.unl.pt

Clear-cut markets for nitrites (NO_2^-) point-of-care tests exist in the food industry, pollution control, clinical diagnostics and biomedicine. At the turn of the 21st century, for instance, rules restricting nitrite concentrations in drinking water and foodstuff were promulgated by international authorities due to the potential risks of methemoglobinemia and cancer, albeit the controversial scientific support of the latter. The extensive use of nitrite precursors as fertilizers is another concern, since it may lead to the contamination of groundwater supplies and disturb the balance of ecosystems. In the field of clinical applications, the detection of nitrites in physiological fluids is commonly used as an index of endothelial nitric oxide (NO) synthase activity.[1] Moreover, NO_2^- quantification has gained an increasing relevance in biomedical research due to its recognition as a central homeostatic species in NO biology and as an important signalling molecule in its own righ.[2] Nevertheless, the levels of nitrites in human plasma have been difficult to measure due to sampling issues and the poor performance of diagnosis methods; analytical bias may be introduced from the initial sampling stage to the final quantification step.[1] As so, the implementation of technology-driven solutions enabling quick and effective readings of NO_2^- would be certainly welcome either in translational medicine or environmental and food control. Over the last decade, our group has been focused on the development of enzyme-based biosensors for nitrites measurement using electrochemical transducers. A number of different strategies using the fast and robust ammonia-forming cytochrome *c* nitrite reductase from *Desulfovibrio desulfuricans* were proposed, all providing high selective and sensitive measurements.[3-10] In this communication, the progress made in this research topic will be shortly reviewed. At a first stage, the enzyme electrodes included synthetic redox mediators to improve electronic communication[3-5] but then, we developed more advanced biosensors using nanostructured surfaces, such as carbon nanotubes[6-8] or tungsten oxide nanoparticles,[9] to facilitate direct electron transfer. Although the proof-of-concept was demonstrated, a few issues had to be resolved before transferring this knowledge to clinical practice or any other market application. Therefore, the 3-electrodes system was fully miniaturized using disposable screen-printed electrodes, the problem of oxygen interference was solved through an enzyme based scavenging system, and finally, quantification assays were successfully made in real samples.[10] Presently, homemade carbon fiber microelectrodes and platinum microelectrode arrays modified with NrfA are being tested as new tools for *in vivo* monitoring of nitrite dynamics in rat brains, targeting a better understand of its role in neurovascular coupling.[11]

References

1. M. G. Almeida, A. Serra, C. M. Silveira, J. J. Moura *Sensors* **2010**, *10*, 11530.
2. N. S. Bryan, J. Losvalzo, eds., Nitrate and Nitrite in Human Health and Disease, **2011**, Springer: New York.
3. S. Da Silva, S. Cosniera, M. G. Almeida, J. J. G. Moura *Electrochem. Commun*. **2004**, *6*, 404.
4. M.G. Almeida, C.M. Silveira, J. J. G Moura *Biosens. Bioelectron.* **2007**, *22*, 2485.
5. H.Chen, C. Mousty, S. Cosniera, C. Silveirac *et al.* *Electrochem. Commun.* **2007**, *9*, 2241.
6. C. M. Silveira, J. Baur, M. Holzinger *et al. Electroanalysis* **2010**, *22*, 2973.
7. C. M. Silveira, S. P. Gomes, A. N. Araújoet al. *Biosens. Bioelectron.* **2010**, *25*, 2026.
8. C. M. Silveira, M. Pimpão, H. A. Pedrosoet *et al. Electrochem. Commun.* **2013**, *35*, 17.
9. L. Santos, C. M Silveira, E. Elangovan *et al. Sens. Actuactors, B,* **2016**, *223*, 186.
10. T. Monteiro, P. R. Rodrigues, A. L. Gonçalveset *et al. Talanta,* **2015**, *142*, 246.
11. C. Dias, T. Monteiro, C. F. Lourenco *et al. J. Neurochem.* **2017**, *142*, 176.

SC20. Electrode Modification by Metal-derived Nanostructures using Interelectrode Material Transfer and Spark Discharges

Jan Hrbac

Institute of Chemistry, Masaryk University, Brno, Czech Republic
jhrbac@atlas.cz

Electrode modification by metal nanostructures or metal precursor nanomaterials is important topic in sensing applications such as amperometric sensing, stripping voltammetry, Surface Enhanced Raman Spectroscopy etc. Generally, the performances of modified electrodes strongly depend on the composition of the modifying layer, its morphology, adherence to the underlying substrate etc. For this reason, various modification procedures and protocols are being continuously developed and optimized. In one of the current research trends, an attention is paid to development of "green and facile" modification procedures, not requiring high consumption of (toxic and/or expensive) chemicals, multiple steps, time consumption etc. yet providing satisfactory performances in desired applications. In this regard, we developed two different techniques leading to metal or metal oxide/hydroxide layers. Interelectrode material transfer method relies on anodic dissolution of target metal electrode and depositing the released anode-derived material onto an electrode to be modified (e.g. silicon plate, carbon fiber microelectrode or screen printed electrode etc.), connected into the circuit as a cathode. To obtain "clean" deposits, the procedure can be carried out in water (i.e., an unsupported medium), provided that sufficient voltage is delivered (5-30 V). The deposition process proceeds via electrochemical reduction, electrophoretic deposition or precipitation induced by pH change in the vicinity of a cathode, the exact mechanism or mechanisms depend on metal and deposition conditions (time, applied voltage). The technique is demonstrated on the case of Ag [1] and Cu [2,3] as well as other metals (Au, Bi, Zn, Sn). The second technique, DC spark discharge is performed by bringing electrode to be modified into close proximity with metal counter electrode and applying high voltage of 800-1200 V between those electrodes, causing a spark to occur, vaporizing small amount of electrode materials. The cloud of materials or their oxidized forms is fast cooled, causing the formation of nanoparticles immobilized on the electrode surface. The method is easy, amenable to automation and controllable by deposition conditions, such as applied voltage. The technique was demonstrated to provide effective modification of electrodes by Bi[3,4], Cu, Ni resp. CuNi alloy[5] and Pt[6].

References

1. V. Halouzka, P. Jakubec, L. Kvitek, V.Likodimos, A. G. Kontos, K. Papadopoulos, P. Falaras, J. Hrbac *J. Electrochem. Soc.* **2013,** *160*, B54.
2. D. Riman, Z. Bartosova, V. Halouzka, J. Vacek, D. Jirovsky, J. Hrbac *RSC Adv.* **2015**, *5*, 31245.
3. V. Halouzka, B. Halouzkova, D. Jirovsky, D. Hemzal, P. Ondra, E. Siranidi, A. G. Kontos, P. Falaras, J. Hrbac *Talanta* **2017,** *165*, 384.
4. D. Riman, D. Jirovsky, J. Hrbac, M. I. Prodromidis *Electrochem. Commun.* **2015**, *50*, 20.
5. D. Riman, A. Avgeropoulos, J. Hrbac, M. I. Prodromidis *Electrochim. Acta* **2015**, *165*, 410.
6. D. Riman, K.Spyrou, Karantzalis, A. E.; Hrbac, J.; Prodromidis, M. I., *Talanta* **2017**, *165*, 466.
7. Z. Bartosova, D. Riman, V. Halouzka, J. Vostalova, V. Simanek, J. Hrbac, D. Jirovsky *Anal. Chim. Acta* **2016**, *935*, 82.

SC21. Wireless Actuation of Conducting Polymers

Bhavana Gupta, Bertrand Goudeau, Alexander Kuhn

University of Bordeaux, ISM UMR CNRS 525, Bordeaux INP, ENSCBP, 33607 Pessac, France
Bhavana.Gupta@enscbp.fr

For the electrochemical actuation of conducting polymers usually an electrical power supply needs to be connecting to the polymer.[1] This can be an important roadblock for several interesting applications. In order to circumvent this problem we suggest using the concept of bipolar electrochemistry.[2-3] In this case electrochemical oxidation and reduction of the polymer can be achieved gradually and without any physical connection to a power supply, leading to wireless bipolar actuation. We validate this concept with a free standing polypyrrole film having intrinsically different morphologies at its two faces. This asymmetry in a single layer of conducting polymer is the key ingredient for efficient bipolar actuation analog to the bilayer structure of a classic actuator.[4] When such a film is immersed in electrolyte solution and a sufficient potential difference is applied between two feeder electrodes, differential shrinking and swelling along the main axis is observed due asymmetric oxidation/reduction at the two extremities of the polymer. The deformation is reversible and its amplitude can be controlled by varying different parameters like the applied voltage, the thickness of the polymer and the composition of the electrolyte. Optimization of these parameters allows to achieve a very efficient bending.[5] This study opens up a completely new branch in the field of conducting polymer actuation due to the wireless mode of action.

References

1. R. H. Baughman, *Science* **2005**, *308*, 63.
2. G. Loget, D. Zigah, L. Bouffier, N. Sojic, A. Kuhn *Acc. Chem. Res.* **2013**, *46*, 2513.
3. S. Tiewcharoen, C. Warakulwit, V. Lapeyre, P. Garrigue, L. Fourier, C. Elissalde, S. Buffière, P. Legros, M. Gayot, J. Limtrakul, A. Kuhn *Angew. Chem. Int. Ed.* **2017**, *in press*, DOI: 10.1002/anie.201707386.
4. F. Garcia-Cordova, L. Valero, Y. A. Ismail, T. F. Otero, *J. Mater. Chem.* **2011**, *21*, 17265.
5. B. Gupta, B. Goudeau, A. Kuhn, **2017**, *submitted*.

T13.

Electrochemical Communication Between Photosynthetic Membranes/Cells and Electrodes for Harvesting Solar Energy

Lo Gorton,[a] Galina Pankratova,[a] Hans-Erik Åkerlund,[a] Per-Åke Albertsson,[a] Dónal Leech[b]

[a] *Lund University, P.O.Box 124, SE-221 00 Lund, Sweden*
[b] *National University of Ireland Galway, Galway, Ireland*

We have shown that flexible osmium redox polymers can work as efficient mediators as well as a convenient immobilisation matrix for a number of both Gram– as well as Gram+ bacteria.[1,2] As a continuation of our work on bacterial cells we have now turned to various photosynthetic organisms/membrane systems. Here we report on electrochemical communication between whole viable photosynthetic bacterial cells[3-5] as well as with eukaryote systems (thylakoid membranes from spinach,[6,7] the eukaryote algae)[8] and electrodes through the use of osmium redox polymers. Here we also report on how to increase the efficiency of the charge transfer from the photosynthetic reaction centres to the electrode and to increase the stability of the system as well as the effect of nanostructuring the electrode surface.[9,10]

References

1. K. Hasan, S. A. Patil, D. Leech, L. Gorton *Biochem. Soc. Rev.* **2012**, *40,* 1330.
2. S. A. Patil, C. Hägerhäll, L. Gorton *Bioanal. Rev.* **2012**, *4,* 159.
3. K. Hasan, S. A. Patil, K. Górecki, C. Hägerhäll, L. Gorton *Bioelectrochemistry* **2013**, *93,* 30.
4. K. Hasan, K. V. Raghava Reddy, V. Eßmann, K.Górecki, P. ÓConghaile, W. Schuhmann, D. Leech, C. Hägerhäll, L. Gorton *Electroanalysis*, **2015**, *27,* 118.
5. K. Hasan, H. B. Yildiz, E. Sperling, P. ÓConghaile, M. A. Packer, D. Leech, C. Hägerhäll, L. Gorton *Phys. Chem. Chem. Phys.* **2014**, *16,* 24676.
6. K. Hasan, Y. Dilgin, S. Cem Emek, M. Tavahodi, H.-E. Åkerlund, P.-Å. Albertsson, L. Gorton *ChemElectroChem* **2014**, *1,* 131.
7. Hamidi, H.; Hasan, K.; Emek, S. C.; Dilgin, Y.; Åkerlund, H.-E.; Albertsson, P.-Å.; Leech, D.; Gorton, L. *ChemSusChem,* **2015**, *8,* 990.
8. K. Hasan, E. Çevik, E. Sperling, M. A. Packer, D. Leech, L. Gorton *Adv. Energy Mater.* **2015**, 1501100.
9. G. Pankratova, D. Pankratov, K. Hasan, H.-E. Åkerlund, P.-Å. Albertsson, D. Leech, S. Shleev, L. Gorton *Adv. Enery Mater.* **2017**, 1602285.
10. H. Kanso, G. Pankratova, P. Bollella, D. Hernandez, L. Gorton, *submitted.*

K26.

High-response Conducting Films Made of Suspensions of Polyaniline-coated Graphene

Jingyuan Chen,*[a] Koichi Jeremiah Aoki[b]

[a]*Department of Applied Physics, University of Fukui, Japan, jchen@u-fukui.ac.jp*
[b]*Electrochemi*stry *Museum, kaoki@u-fukui.ac.jp*

A fast response is required for amperometric electrochemical sensors. A technique of enhancing the response is to increase electric conductivity of films. Polyaniline (PANI) and reduced graphene oxide particles (RGO) composite films provide charge density and current large enough for supercapacitors.[1] It is interesting to examine a role of PANI and RGO for the fast response. Here, we are concerned with finding these mechanisms by use of PANI-RGO suspension,[2] of which particle-particle interaction can be controlled in the preparation. Flaky particles of PANI-RGO with rectangular size of 1.0-1.5 µm are dispersed in aqueous solution. The PANI- RGO film made of the suspension forms a self-standing, elastic, conductive film.[3] Film exhibited faster redox conversion than the PANI film did. A reason of the enhancement of the conversion rate was searched by examining the growth rates of the conducting zone when the reduced composite were oxidized electrochemically from one end film, as shown in Fig.1. The length, x, of the growing conducting zone, was plotted against the time, t, of applying the oxidation potential, as shown in Fig. 2. The morphology of the cross section (Fig. 1) indicates that the reaction occurs at rough surface area rather than the projected area. An increase in ϕ (= w_{RGO} / ($w_{\mathrm{RGO}} + w_{\mathrm{PANI}}$)) necessarily increases the net surface area to enhance j_0. We estimate the surface roughness quantitatively. The growth rate was modeled with the oxidation at the Tafel-typed rate, which was restrained by the IR-drop between the conducting front and the electrode. The growth length was expressed by a time-dependent non-linear differential equation. The numerical solution allowed us to analyze the experimental data of the time variation of the growth length. RGO functions as an increase in the rough surface area of the oxidation rather than electric percolation, enhancement of conductivity and catalytic effects.

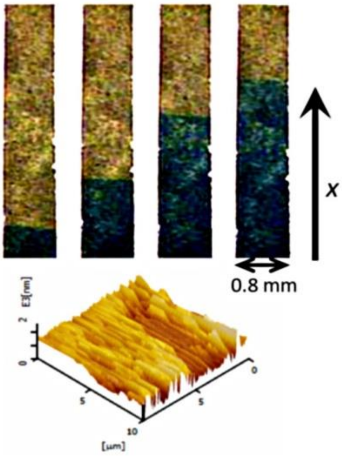


Fig. 1 Photographs of PANI-RGO films taken at indicated times after 0.4 V is applied. The cross section of the PANI-RGO film observed by AFM.

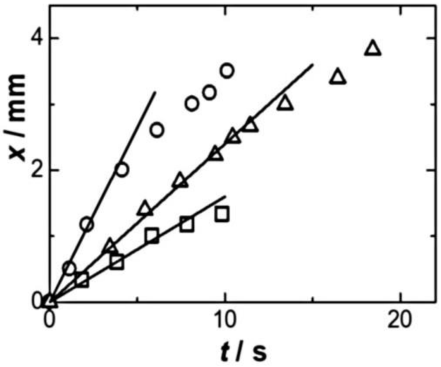


Fig. 2 Variations of the growth length of the conducting zone with the time of applying potentials of (circles) 0.6, (triangles) 0.5 and (squares) 0.4 V vs. Ag|AgCl for the film at ϕ = 0.30.

References

1. Z. Gao, F. Wang, J. Chang, D. Wu, X. Wang, X. Wang, F. Xu, S. Gao, K. Jiang *Electrochim. Acta,* **2014**, *133*, 325.
2. J. Chen, X, Zeng, K. J. Aoki, T. Nishiumi *Int. J. Chem.* **2015**, *7*, 1.
3. X. Zeng, K. Aoki, J. Chen *Electrochim. Acta*. **2017**, *228,* 125.

This page intentionally left blank

Poster Session

Saturday, November 4
20:00-22:00

P01. One Electrolyte Based Glucose/Oxygen Electric Power Biodevice with an Operating Voltage Exceeding 1.24 Volt

Olga Aleksejeva,[a] Elena Gonzalez-Arribas,[a] Chiara Di Bari,[b] Antonio L. De Lacey,[b] Marcos Pita,[b]
Roland Ludwig,[c] Miguel D. Toscano,[d] and Sergey Shleev[a]

[a] *Biomedical Science, Malmö University, Malmö, Sweden*
[b] *Instituto de Catálisis y Petroleoquímica, Madrid, Spain*
[c] *Department of Food Sciences and Technology,*
BOKU−University of Natural Resources and Applied Life Sciences Vienna, Wien, Austria
[d] *Novozymes A/S, Bagsværd, Denmark*
olga.aleksejeva@mah.se

Rapid technological developments in recent years have opened up many possibilities to construct personal electronic/electromechanical devices, including those for biomedical applications. However, such devices need to be powered by efficient electric power sources[1] that, in the case of implanted biomedical devices,[2] also need to be long-lasting, safe, stable, and biocompatible. While fuel cells have the potential to address this problem, and have been researched for several decades, one of their main drawbacks is a low operating voltage, which is thermodynamically limited to 1.24 V in the case of glucose/oxygen devices.[3] Here we report a proof-of-principle demonstration of a high-voltage biodevice that is capable of generating sustained electric power at voltage, which exceeds the thermodynamic limit. Due to the interplays between faradaic and non-faradaic electrochemical processes, as well as between ionic and electronic conductivities, the biodevice, consisting of several self-charging biosupercapacitors connected in series and operating in the same electrolyte in a pulse mode, provides apparently unreachable open-circuit and operating voltages. Owning to redox enzymes, biocatalysts par excellence, individual biosupercapacitors are self-charged, and after that, the complete biodevice is externally discharged. Our results demonstrate proof-of-principle operation of a high-voltage biological power source working in an authentic human blood stream, which we anticipate to be a starting point for the design of high performance implanted power sources.

Acknowledgements

This work was financially supported by the Swedish Research Council (project 2013-6006).

References

1. N.-S. Choi, Z. Chen, S. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. Nazar, J. Cho, P. Bruce *Angew. Chem. Int. Ed.* **2012**, *51*, 9994.
2. E. Meng, R. Sheybani *Lab Chip* **2014**, *14*, 3233.
3. S. Shleev *ChemPlusChem*, **2017**, *82*, 523.

P02. Spray-Coating as a Versatile Tool for Electrode Surface Modification – from Nanostructured Electrodes to Enzyme Based Sensors

Tim Bobrowski, Adrian Ruff, Felipe Conzuelo, Fangyuan Zhao,
Kirill Sliozberg, Wolfgang Schuhmann

Analytical Chemistry – Center for Electrochemical Sciences (CES),
Ruhr-Universität Bochum, Universitätsstr. 150, D-44870 Bochum, Germany
tim.bobrowski@rub.de

Electrochemical biodevices (*e.g.* biosensors and biofuel cells) do not only rely on the general stability and activity of the utilised biocatalyst but also on the architecture of the entire electrode. In particular, the choice of suitable electrode surface structuring, enzyme immobilisation technique, as well as the co-immobilization of electron mediators is crucial for a highly sensitive and efficient sensing system. Recently, we presented the fabrication of a membrane-free glucose/O_2 powered enzymatic fuel cell, based on transparent nanostructured indium tin oxide (ITO) electrodes prepared from a spray-coating process.[1] Compared to ITO nanoparticle (NP) based electrodes prepared by drop-casting, the performance and stability of the glucose/oxygen converting device was significantly improved by utilising ITO-NP based electrodes prepared via a spray-coating process. Optimisation of the spray-coating process for the preparation of the electrodes led to highly electrochemically active surface areas with increased porosity, thus enhancing the catalytic currents due to higher biocatalyst loading and decreasing the lower detection limit for glucose. In this work, we used a specifically designed spray-coating system as a tool for electrode surface modification. In brief, the computer controlled system consists of a 3D moveable air-pressure nozzle connected to a pump which transports the sample solution into the spray-tip. The automated process ensures the formation of homogeneous and reproducible electrode surfaces. Moreover, the system cannot only be used for the preparation of nanostructured electrode surfaces, such as ITO-NP based electrodes, but also allows spraying of enzyme and polymer solutions. In this way, even a large-scale modification of electrodes becomes possible. After further modification of ITO-NP structured electrodes by layered spraying of glucose oxidase embedded in an osmium complex modified polymer onto the porous surface, such electrodes were utilised in a self-powered glucose biosensor operated by charge/discharge of a Nernstian biosupercapacitor.[2] As a second example, the development and optimisation of meso- and macro-porous ITO based electrodes will be discussed. A mixture of ITO nanoparticles and spherical, monodisperse polymer beads acting as template for pore formation was sprayed onto flat electrodes. The polymer beads were removed by calcination of the material which generates macro-pores of the size of the polymer beads. The porous structure ensures an effective wiring of the redox polymer and minimises limitations due to a slow electron transfer within the polymer by ensuring short electron transport pathways based on the 3D structure of the electrode. Our results demonstrate the high flexibility of the developed spray-coater not only for surface structuring but also for complete modification of entire electrode architectures with enzymes wired in hydrogels with applications in fuel cells, biosupercapacitors or self-powered biosensors.

Acknowledgments
This work has been financially supported by the European Commission (PEOPLE-2013-ITN-607793) and the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft (DFG).

References

1. E. González-Arribas, T. Bobrowski, C. di Bari, K. Sliozberg, R. Ludwig, M.D. Toscano, A. L. de Lacey, M. Pita, W. Schuhmann, S. Shleev *Biosens. Bioelectron.* **2017**, *97*, 46.
2. D. Pankratov, F. Conzuelo, P. Pinyou, S. Alsaoub, W. Schuhmann, S. Shleev *Angew. Chem. Int. Ed.* **2016**, *55*, 15434.

P03. Towards a Better Understanding of Target-aptamer Binding in Homogeneous Assays

Fabio Bottari,[a,c] Elise Daems,[c,d,e] Frank Sobott,[b]
Pieter Van Wielendaele,[b] Anne-Marie Lambeir,[a] Karolien De Wael

[a] AXES Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium
[b] Medical Biochemistry Group, Department of Pharmaceutical Sciences,
University of Antwerp, Antwerp, Belgium
[c] BAMS Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium
[d] Astbury Centre for Structural Molecular Biology, University of Leeds, Leeds LS2 9JT, UK
[e] School of Molecular and Cellular Biology, University of Leeds, Leeds LS2 9JT, UK
fabio.bottari@uantwerpen.be

In the last couple of years, aptamers have been used as powerful tools in medicine, molecular biology and analytical chemistry. The high binding affinity and specificity of aptamers is the prerequisite for many applications; therefore the detailed characterization of their binding behavior is the most important step after selection. The binding mechanism of each aptamer is different as well as the secondary and tertiary structure formed. However very few studies tried to understand whether the detection strategy employed influences the binding affinity or the mechanism. For this reason a comparative study of homogeneous binding of an ampicillin aptamer was performed[1]. Ampicillin is an important Beta Lactam antibiotic commonly used both in human and veterinary medicine. Nowadays residues in the environment are a major concern, especially for the insurgence of antimicrobial resistance. The authors used a colorimetric gold nanoparticles (AuNPs) assay for the detection of the binding event. We reproduced the experiments reported and compared the result with two innovative and very sensitive techniques, useful to study molecular interactions in homogeneous solutions, Isothermal Titration Calorimetry (ITC) and Native Electrospray Ionization Mass Spectrometry (ESI-MS). Both techniques were already successfully used to characterize binding constant of aptamers for many different targets[2-3]. Surprisingly both techniques were not able to detect the binding event, while the AuNPs assay worked as reported. The fact that the aptamer is interacting with the surface of the nanoparticles seems to have an effect on the binding mechanism. The question is still under investigation but these results cast some shadows on our understanding of how aptamer-target interactions really works and how new aptamers should be characterized.

References

1. K. Song, E. Jeong, W. Jeon , M. Cho, C. Ban *Anal Bioanal Chem*, **2012**, *402*, 2153.
2. M. A.D. Neves, O. Reinstein, M. Saad, P. E. Johnson *Bioph. Chem*., **2010**, *153*, 9.
3. B. Gülbakan *Anal. Methods* **2015**, *7*, 7416.

P04. Electrode-modified with Nanoparticles Composed of 4,4'-Bipyridine-Silver Coordination Polymer for Sensitive Determination of Hg(II), Cu(II) and Pb(II)

Ana Chira,[a,b] Bogdan Bucur,[a] Madalina Petruta Bucur,[a] and Gabriel Lucian Radu[b]

[a] *Centre of Bioanalysis, National Institute of Research and Development for Biological Sciences, 296, Splaiul Independentei, Bucharest 060031, Romania.*
[b] *Faculty of Applied Chemistry and Materials Science, Politehnica University of Bucharest, 1-7, Polizu, Bucharest 011061, Romania. E-mail: gl_radu@chim.upb.ro*
ana_chira@yahoo.com

A glassy carbon electrode modified with nanoparticles of 4,4-bipyridine-silver coordination polymer was used for highly sensitive analysis of heavy metals (Hg(II), Cu(II) and Pb(II)) by differential pulse voltammetry. The coordination polymers were immobilized on the glassy carbon electrode surface via an organic layer that contains phenylmethyl-4,4'- bipyridinium and coordinated silver ions. The modification method is rapid (an electrode is produced in less than 30 min); electrodes are stable and can be used for the analysis of at least 70 real samples.

A glassy carbon electrode (GCE) modified with nanoparticles composed of a 4,4'-bipyridine silver coordination polymer (CP) were applied to the sensitive differential pulse voltammetric analysis of the ions Hg(II), Cu(II) and Pb(II).

The coordination polymer was prepared by mixing a solution of silver nitrate and 4,4'-bipyridine at room temperature. The surface of the GCE was modified with an organic layer of synthesized 1-[(4-nitrophenyl)methyl]-4,4'-bipyridinium and silver ions, which caused the binding of the added Ag-bipy-CP. Anodic (oxidative) peaks of the electrode were at +300 mV for Hg(II), -70 mV for Cu(II), and at -540 mV for Pb(II) [versus Ag/AgCl]. The detection limits were 0.09 mg/L Hg(II), 0.71 mg/L Cu(II) and 2.3 mg/L Pb(II). Relative standard deviation was 3.2% at a level of 4 mg L of Hg(II) for n=10.

Importantly, the sensitivity and stability of the developed modified electrodes allowed their used for determination of Hg(II) in spiked fish samples and Cu(II), Pb(II), and Hg(II) in spiked plant samples with good recovery 90 to 108%.

This study demonstrates the utility of coordination polymers for the development of electrochemical sensors and opens a new area of applications for these versatile materials.

References

1 A. Chira, B. Bucur, M. P. Bucur, G. L. Radu *New J. Chem.* **2014**, *38*, 5641.

P05. Driving Photosystem I with an Enzyme: Competitive Wiring of Photosystem I in a 3D Biohybrid Electrode Arrangement for Light-switchable Bioelectronics

Dmitri Ciornii,[a] Marc Riedel,[a] Kai Stieger,[a] Sven Feifel,[a] Mahdi Hejazi,[b]
Silke Leimkühler,[c] Athina Zouni,[b] Fred Lisdat[a]

[a] *Biosystems Technology, Institute of Applied Life Sciences,*
Technical University of Applied Sciences Wildau, Hochschulring 1, 15475 Wildau, Germany
[b] *Biophysics of Photosynthesis, Institute for Biology,*
Humboldt-University of Berlin, Philippstrasse 13, Haus 18, 10115 Berlin, Germany
[c] *Institute for Biochemistry and Biology, University of Potsdam,*
Karl-Liebknecht Str. 24-25, H.25, Golm, D-14476, Germany

The goal of the present study was to construct an all-protein based controllable self-sufficient biohybrid system with multiple features by using redox proteins and enzymes. We report that our assembly strategy has been successful and the developed system has shown functionality and reproducibility. Briefly, we have used a photosensitive bio-component - photosystem I (PSI) as a central building block, an electron supplier - the redox enzyme human sulfite oxidase (hSOX) and a molecular wire - cytochrome *c* (cyt *c*). All compounds have been immobilized within a 3D electrode (inverse opal micro-ITO). Three types of catalytic reactions, the photocatalytic, the electrocatalytic and the biocatalytic one, have been tuned to act in such a way that the electron flow can be switched (see fig. 1): Upon illumination charge carriers are generated within PSI followed by withdrawing electrons from the electrode via cyt *c*, whereas upon addition of sulfite (substrate of hSOX) electron flow from the electrode can be diminished by means of sulfite conversion and thus, enabling electron flow through a "competitive pathway". Here, cyt *c* serves as "switching point" which can be reduced either from electrode (if no sulfite is present) or by hSOX (if sulfite is added). The self-sustainable character of the system has been demonstrated by means of potentiometric experiments. In conclusion, our system shows four interesting features: (i) it can be used as a kind of capacitor with high surface area, (ii) electron pathways can be switched "on" and "off" on demand, (iii) photosensing of sulfite is feasible and (iv) potential measurements verify the self-driven character of the system.

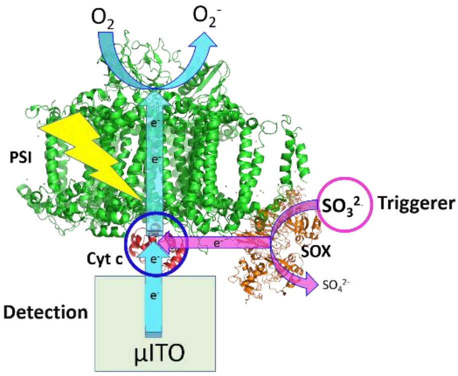


Figure 1. Schematic illustration of the concept and electron pathways in the biohybrid architecture.

P06. Electrode Modification by Bismuth Ion Implantation

Sonivette Colón-Rodríguez,[a] Gourav Bhowmik,[c] Mengbing Huang,[b,c] Gerd U. Flechsig[a]

[a] *University at Albany-SUNY, Department of Chemistry, Albany, NY 12222, USA*
[b] *University at Albany, SUNY, Ion Beam Lab, Albany, NY 12222, USA*
[c] *SUNY Polytechnic Institute, College of Nanoscale and Engineering, Albany, NY 12203, USA*
scolon-rodriguez@albany.edu

Bismuth film electrodes have been widely studied due to their advantages in increasing hydrogen overvoltage towards a more cathodic potential range, less sensitivity to dissolved oxygen and as a nontoxic alternative for the replacement of mercury electrodes.[1,2] However, it is cumbersome to prepare the Bi film electrochemically in-situ or ex-situ. Here we present a new type of bismuth-modified gold surface on screen-printed electrodes (BiAuSPE) obtained by ion implantation. An Extrion 400 Ion Implanter (Varian) was used for the bismuth implantation. Bismuth ions ($^{209}Bi^{+}$) impinged on the gold surface of the screen-printed electrodes at 30 keV with a dose of $1.3\ x10^{16}$ ions/cm^{2} with ca. 40% Bi ions being implanted. Characterization of the electrochemical behavior in comparison with our heated Bi film electrode[1] was performed using cyclic voltammetry in 0.2 M sodium acetate buffer at pH 5. The bismuth-implanted gold electrode showed a wider cathodic potential range in comparison with the bare gold screen-printed electrode. Measurements at 100 mV/s scan rate were performed at room temperature (23 ^{o}C) in a three-electrode electrochemical cell using Ag/AgCl|3 M KCl and glassy carbon as reference and counter electrode, respectively. Figure 1A illustrates the -400 mV shift of the negative end of the potential window using the bismuth-implanted electrode in comparison with a bare screen-printed gold electrode. Due to the observed hydrogen overpotential, stripping voltammetry measurements starting at -1.2 V may be useful for heavy metal analysis of such as zinc and cadmium.[3]

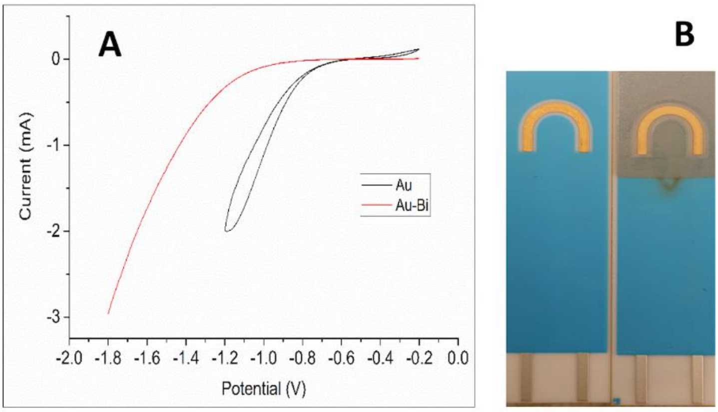


Figure 1. [A] Cyclic voltammetry measurements in 0.2 M sodium acetate buffer (pH 5) at room temperature (23 ^{o}C) at screen-printed gold electrode (black) and compared with bismuth-implanted electrode (red). [B] Gold loop electrode before (left) and after (right) bismuth implantation.

References

1. M. Jacobsen, H. Duwensee, F. Wachholz, M. Adamovski, G.-U. Flechsig *Electroanalysis* **2010**, *22*, 1483.
2. S. M. Skogvold, Ø. Mikkelsen *Electroanalysis* **2008**, *20*, 1738.
3. M.R Palomo-Marín, F. Rueda-Holgado, J. Marín-Exposito, E. Pinilla-Gill *Talanta*, **2017**, *175*, 313.

P07. Studies of Surface Effects to Enhance Sensitivity of Ion-selective Electrodes for Bicarbonates

S. Dabrowska, J. Migdalski, A. Lewenstam

AGH University of Science and Technology, Faculty of Materials Science and Ceramics,
Mickiewicza 30, 30-059 Krakow, Poland

Poly(vinyl chloride), PVC, is the most frequently used polymer in the present design of ion-selective electrode membranes. This is mainly due to its chemical inertness and high compatibility with various plasticizers. In our previous work, the bicarbonate ion-sensor was prepared by incorporation of a quaternary ammonium salt as an ion-exchanger into the polymer matrix of PVC.[1] The selectivity sequence was close to the Hofmeister series. However, the use of these sensors for determination of bicarbonate ions in real samples is limited by the low selectivity to bicarbonate ions over chlorides ions.

To improve the selectivity of bicarbonate potentiometric membranes it is necessary to develop dedicated new formulations and architectures. This work is focused on the use of various polymers as the membrane components or discriminating layers, e.g., room-temperature-vulcanizing silicone rubber, Nafion, poly(ether ether ketone) and gel polystyrene cross linked with divinylbenzene. The materials were evaluated in ionophore free ion exchanger membrane.

The membranes studied exhibit similar response for primary hydrogen carbonate ions as for known the conventional PVC matrix membranes. However, substantially reduced interference of chloride ions was achieved. The influence of chloride ions was additionally diminished by so-called kinetic discrimination, i.e., by performing the measurements in the presence of chlorides over a short time.

Acknowledgments

National Science Centre (NCN, Poland) financial support via research grant no. 2014/15/B/ST5/02185 is acknowledged.

References

1. S. Dabrowska, J. Migdalski, A. Lewenstam *Electroanalysis,* **2017**, *29*, 140.

P08. Controlled Labelling of an Electrochemical Peptide-based Sensor Aiming Ghrelin Receptor Agonists Detection

George M. Dănilă,[a] Lucian G. Zamfir,[b] Mihaela Puiu,[b] Camelia Bala[a, b]

[a] Department of Analytical Chemistry, University of Bucharest, Bucharest, Romania
[b] Laboratory for Quality Control And Process Monitoring,
University of Bucharest, Bucharest, Romania
madalin.danila@drd.unibuc.ro

Peptides have been used as tools in biological analysis and development of new biosensors for multiple reasons including the diversity of structures and high selectivity substrates for enzymes, receptors and antibodies[1]. In contrast, peptide-based biosensors coupled with electrochemical detection often display voltammetric baseline fluctuations because the recognition peptide in the unbound state doesn't possess a structure-free conformation[2] and the secondary structure of the peptide amino acid chain cannot be controlled[3]. Moreover, redox labelling on the recognition peptide could determine changes in the interaction with antibody / enzyme or could block the amino acid residues responsible for recognition. Another drawback is the relative low stability in time, because often recognition peptides cannot adopt a conformation like helix proteins, able to form a compact layer. To overcome these disadvantages, we report here a new strategy for the development of an electrochemical peptide-based sensor. We first immobilized a short helical support peptide (SP) on the surface of a gold electrode together with 1,6-hexanedithiol (HDT) to obtain a self-assembled monolayer with a highly ordered structure[4]. We employed Methylene Blue (MB)-succinimidyl ester to tag several nucleophilic groups from the peptide backbone. In this way, we ensured an efficient electron transfer from MB to gold surface through the helix-like structure of the support peptide. The free carboxylic groups from the support peptide were available for binding the agonist recognition peptides for the Growth Hormone Secretagogue Receptor (or ghrelin receptor, GHS-R) protein. As recognition peptides we used two Growth Hormone Releasing peptides: GHRP-5 (small peptide, 5 amino acid residues, and 770 Da) and CJC-1295 (30 amino acid residues, 3368 Da, conjugated with a Drug Affinity complex containing maleimide). GHRP-5 was covalently bound to the support peptide and CJC-1295 through maleimide-thiol coupling and in the presence of GHS-R (58 kDa), we would see a signalling-on and signalling–off response, depending on the labelling protocol. This novel and label-controlled approach could serve as a general strategy to obtain high-stability redox-peptide monolayers for the detection of both GHS-R peptidic and non-peptidic ghrelin agonists through a competitive assay.

References

1. Q. Liu, J. Wang, B.J. Boyd *Talanta*, **2015**, *136*, 114.
2. F. Ricci, A.J. Bonham, A.C. Mason, N.O. Reich, K.W. Plaxco *Anal.Chem.* **2009**, *81*, 1608.
3. E. Gatto, L. Stella, F. Formaggio, C. Toniolo, L. Torenzelli, M. Venanzi, *J. Pept. Sci.* **2008**, *14*, 184.
4. M. Puiu, A. Idili, D. Moscone, F. Ricci, C. Bala *Chem. Commun.* **2014**, *50*, 8962.

P09. **Suspension of Silver Nanoparticles on Rotating Ring-disk Electrode**

J. Dolinska, M. Holdynski, M. Opallo

Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland
jdolinska@ichf.edu.pl

Silver nanoparticles – the most important type of nanoparticles due to multitude of application, best known for antibacterial properties,[1,2] and also coloring properties.[3] Due to growing popularity and variety of uses the release of nanoparticles to the environment[4] is growing rapidly. In the laboratory scale it is easy to dissolve silver nanoparticles in chemical/electrochemical way producing Ag^+ cations. Spontaneous formation of Ag^+ cations also occurs in environment and this is the reason, why environmental monitoring of (nano)pollution is important. Here we would like to demonstrate a simple, fast and efficient way of Ag nanoparticles detection based on their electrochemical oxidation at rotating disc electrode. to not only determination in potable water of presence nanoparticles. This method is different that proposed earlier based on electrooxidation of Ag nanoparticles on ultramicroelectrode in quiescent conditions.[4] The proposed method can be also applied for Ag nanoparticles removal from the liquid environment.

References

1. G. A. Martínez-Castañón, N. Niño-Martínez, F. Martínez-Gutierrez, J. R. Martínez-Mendoza, F. Ruiz *J. Nanopart. Res.* **2008**, *10*, 1343.
2. C. Marambio-Jones, E. M. V. Hoek *J. Nanopart. Res.* **2010**, *12*, 1531.
3. Shahid-ul-Islam, B. S. Butola, F. Mohammad *RSC Adv.* **2016**, *6*, 44232.
4. E. J. E. Stuart, N. V. Rees, J. T. Cullen, R. G. Compton *Nanoscale*, **2012**, *5*, 174.

P10. Graphene-gold Clusters Hybrid Materials for the Immobilization of Redox Enzymes

Maciej Dzwonek, Agnieszka Więckowska, Renata Bilewicz

Faculty of Chemistry, University of Warsaw, 02-093 Warsaw, Poland
mdzwonek@chem.uw.edu.pl

The properties of metal nanoparticles depend mainly on composition, size and shape of the examined structures. Gold nanoparticles of 2 nm diameter (gold clusters) show significant differences in optical, electrical or chemical properties compared with the larger nanoparticles (> 2.5-3.0 nm core diameter). Gold clusters with very low polydispersity index (PI) are often redox electroactive due to their ability to accumulate the charge on the surface. According to these features, gold clusters could be used for the enhancement of electrical conductivity of solid supports as well as for the immobilization of enzymes.[1] This project is devoted to the construction of hybrid material composed of electrochemically reduced graphene oxide layers and gold clusters used for anchoring of enzyme molecules. Gold clusters were synthesized using the method proposed by Maran and coworkers[2] modified in our group in order to attach additional functional group to the surface of gold clusters for effective binding the protein.[3] We use different quinone derivatives for the modification of the gold clusters surfaces and present the microscopic, spectroscopic and electrochemical characteristics of the obtained clusters. Graphene oxide (GO) layers were obtained using modified Hummers-Offeman method[4,5] and further electrochemically reduced,[6] to obtain reduced graphene oxide (rGO) layers on the glassy carbon electrode surface. The matrix will be used to immobilize enzyme molecules effectively and retain their activity.

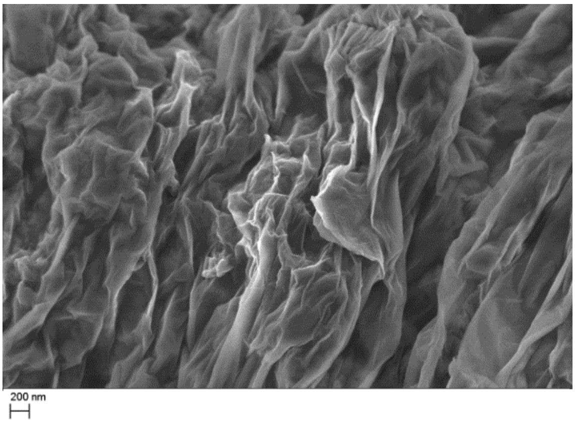


Figure 1. The SEM image of reduced graphene oxide deposited on glassy carbon electrode.

References

1. B. M. Quinn, P. Liljeroth, V. Ruiz, T. Laaksonen, K. Kontturi *J. Am. Chem. Soc.* **2003**, *125*, 6644.
2. T. Dainese, S. Antonello, J. A. Gascón, F. Pan, N. V. Perera, M. Ruzzi, A. Venzo, A. Zoleo, K. Rissanen, F. Maran *ACS Nano* **2014**, *8*, 3904.
3. A. Wieckowska, M. Dzwonek *Sens. Actuators, B* **2016**, *224*, 514.
4. W. S. Hummers, R. E. Offeman *J. Am. Chem. Soc.* **1958**, *80*, 1339.
5. D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour *ACS Nano* **2010**, *4*, 4806.
6. C. Di Bari, A. Gonti-Urtiaga, M. Pita, S. Shleev, M. D. Toscano, R. Sainz, A. L. De Lacey *Electrochim. Acta* **2016**, *191*, 500.

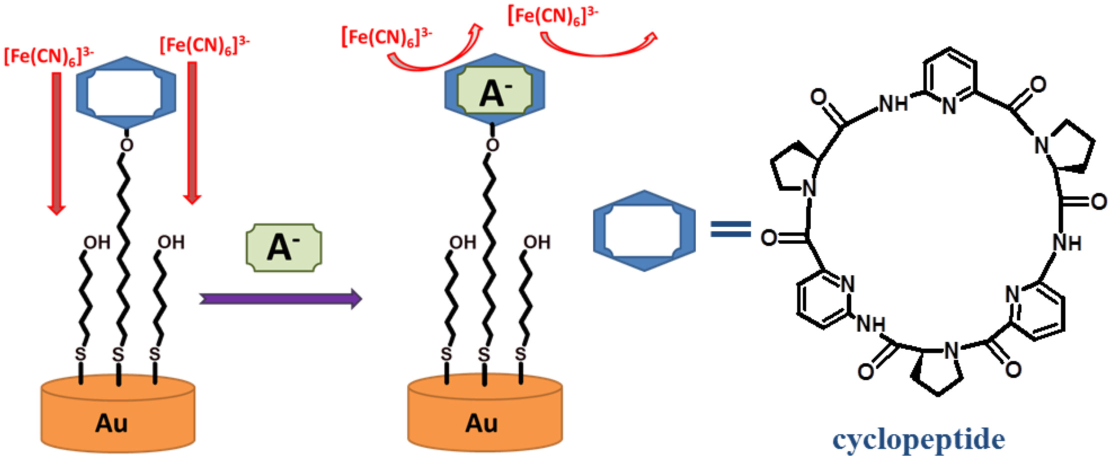
P11. Ion Channel Mimetic Sensor Incorporating Cyclopeptide Designed for Anion Recognition in Aqueous Solutions

Piotr Gołębiewski,[a] Fabian Sommer,[b] Stefan Kubik,[b] Hanna Radecka,[a] Jerzy Radecki[a]

[a] Institute of Animal Reproduction and Food Research,
Polish Academy of Sciences, Olsztyn, Poland
[b] Fachbereich Chemie- Organische Chemie,
Technische Universitat Kaiserlautern, Kaiserlautern, Germany
p.golebiewski@pan.olsztyn.pl; j.radecki@pan.olsztyn.pl

In recent decades, a lot of examples of receptors for anion recognition have been designed. But for most of them influence water molecules decreases their affinity of anion binding properties in aqueous solutions.[1] The anions play the important role in physiological processes occurring in the human body, as well as in the natural environment. Thus, the development of sensitive and selective anion sensors working in water media is especially important.[2]

Here, we present ion channel system, which can fulfil this need. The gold electrodes were modified with unique cyclopeptide responsible for anion recognitions *via* creation of hydrogen bonds.[1] The cyclopeptide - anion recognition process has been explored using Cyclic Voltammetry (CV) and Osteryoung Square-wave voltammetry (OSWV). In the proposed system, the binding of anions to receptor molecules changes the charge of the analytically active layer. This influence on the accessibility of redox marker present in the solution towards electrode surface (Scheme 1). Obtained results shows that presented sensor can selective determine SO_4^{2-} ions at pM level in aqueous solutions. In the presence of interfering ions such as Cl^- and $H_2PO_4^-$ lower analytical signals have been observed. Taking into account these parameters, proposed analytical system could be suitable for environmental monitoring, as well as medical or food sample control.



Scheme 1. Illustration of working principle of ion-channel mimetic sensor.

Acknowledgements
This work was supported by project: National Science Centre, Poland, No 2016/21/B/ST4/03834.

References

1. S. Kubik *Chem. Soc. Rev*. **2009,** *38*, 585.
2. N. H. Evans, P. D. Beer *Angew. Chem. Int. Ed.* **2014**, *53*, 11716.

P12. Synthesis and Properties of Nanostructured Polyazulene

Emilia Grądzka, Patrycja Makowska, Krzysztof Winkler

Institute of Chemistry, University of Bialystok, Poland
emilia@uwb.edu.pl

Conducting polymers have attracted great deal of interest due to their high specific capacitance, easy way of synthesis, relatively good stability, and low cost of materials.[1-3] So far, polyaniline, polypyrrole, and polythiophene have received considerable attention due to their good redox reversibility and chemical stability.[3-7] Apart from these *p*-type conducting system polyazulene exhibits also very promising properties.[8] In can be formed electrochemically and chemically. Electrochemical polymerization results in formation of uniform polymeric structure. In the case of chemical synthesis, the nanostructured material can be prepared.

Nanostructured polyazulene was synthesized in both, template-free and template assisted methods. The template-free chemical synthesis carried out in solution containing monomer and oxidizing agent results in formation of spherical particles 50-400 nm in diameter (Fig.1). In hard-template method, spherical mesoporous silica was used. This method allows to control shape and porosity of synthesized materials. Surfactant-assisted polymerization was also used for the preparation of polyazulene nanoparticles. The influence of synthesis conditions on morphology and electrochemical properties of polymeric nanostructures was studied. Moreover, electrochemical properties with special regard to capacitance properties of chemically and electrochemically prepared polyazulene were also investigated.

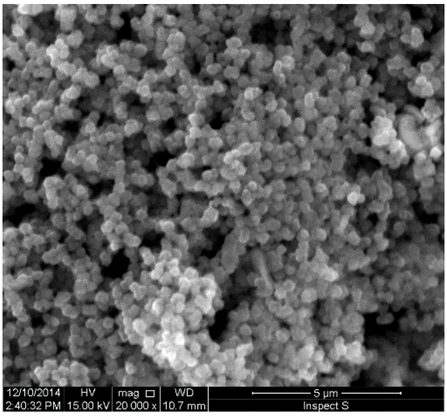


Figure 1. SEM images of polyazulene nanoparticles.

References

1. E. Frackowiak, F. Beguin *Carbon* **2002**, *40*, 1775.
2. K. Jurewicz, S. Delpeux, V. Bertagna, F. Beguin and E. Frackowiak *Chem. Phys. Lett.* **2001**, *347,* 36.
3. H. Wang, J. Lin, Z.X. Shen *Journal of Science: Advanced Materials and Devices* **2016**, *1*, 225.
4. C. Peng, D. Hu, G. Z. Chen *Chem. Commun.* **2011**, *47,* 4105.
5. M. S. Kim, J. H. Moon, P. J. Yoo, J. H. Park *J. Electrochem. Soc.* **2012**, *159*, A1052.
6. B. C. Kim, J. M. Ko, G. G. Wallace *J. Power Sources* **2008**, *177*, 665.
7. K. Lota, V. Khomenko, E. Frackowiak *J. Phys. Chem. Solids* **2004**, *65*, 295.
8. E. Grodzka, K. Winkler, B.M. Esteban, C. Kvarnstrom *Electrochim. Acta* **2010**, *55*, 970.

P13. Enzymatic Thin Layer Flow-Cell with Screen-Printed Electrodes and Lipidic Cubic Phase: Approach for Simple Miniaturized Biofuel Cell

V. Grippo,[a] S. Ma,[b] R. Ludwig,[b] D. Hernandez Santos,[c] R. Bilewicz [a]

[a] *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*
[b] *Department of Food Sciences and Technology, Food Biotechnology Laboratory, BOKU – University of Natural Resources and Life Sciences, Muthgasse 18, 1190 Vienna, Austria*
[c] *Dropsens, Parque Tecnológico de Asturias, Edificio CEEI, 33428 Llanera, Spain*
v.grippo@chem.uw.edu.pl

Biofuel cells (BFC) are potential power sources for biological applications especially for biosensors and implantable devices so the past years have witnessed an exponential surge in research related to biofuel cell.[1] Enzyme-modified electrodes show great advantages to be used in fuel cells because of their low cytotoxicity, biocompatibility and facile exchange of electrons between enzyme active sites and appropriately prepared electrode surfaces. Enzymes are highly specific for the substrate so there is no need of membranes between electrodes. A typical enzymatic biofuel cell consists of an enzyme functionalized bioanode and biocathode.

Here we present a miniaturized BFC with screen-printed electrodes integrated in a fully disposable flow cell. Compared to the traditional Flow Analysis device with electrochemical detection, the thin layer flow cell (TLFCL) does not need any pretreatment or electrodes polishing and it is easy to handle.

Carbon-based electrodes were modified by drop casting graphene and MWCNTs covalently naphthylated[2] to improve enzymes direct communication with electrodes and increase the working surface area of the electrodes. D-Fructose Dehydrogenase from *Gluconobacter sp.* (FDH) and *Corynascus Thermophilus* Cellobiose Dehydrogenase (*Ct*CDH) were used as anodic enzymes and *Myrothecium verrucaria* Bilirubin Oxidase (*Mv*BOd) as a biocathode to build a sugar/O_2 BFC. The electrodes were located in a TLFCL and a sugar solution (50 mM MOPS buffer 100 mM NaCl and 30 mM $CaCl_2$, pH 6.0) in atmospheric air was flowed. Alternatively, a layer of lipidic cubic phase containing only electrolytes and sugars, was placed between the enzymes modified electrodes and provided the supporting electrolyte in the liquid crystalline state. A variable load (R= 1kΩ to 10 MΩ) was applied to the circuit and parameters of the fuel cell were measured.

The changes of potential during the work of biofuel cell of each electrode were monitored versus a *pseudoreference* Ag electrode present in the TLFCL (E = - 0.071 V *vs.* Ag/AgCl KCl sat.).[2] The substrate concentration was investigated and also optimized.

References

1. A. J. Bandodkar, J. Wang *Electroanalysis* **2016**, *6*, 1188.
2. K. Stolarczyk, D. Łyp, K. Żelechowska, J. F. Biernat, J. Rogalski, R. Bilewicz *Electrochim. Acta* **2012**, *79*, 74.

P14. Nafion-graphene Nanoplatelets Ultra-thin Composite Langmuir-Schaefer films: Charge Transport Properties and Electrochemiluminescence Applications

Sandra SHA. Hernandez Aldave, Paolo PB. Bertoncello

College of Engineering, Swansea University, Bay Campus, Swansea SA1 8EN, United Kingdom.
sandra_19_hernandez@hotmail.com

A Nafion-Graphene Nanoplatelets (N-GNPs) nanocomposite dispersion was utilized to fabricate N-GNPs ultra-thin films using the Langmuir-Schaefer (LS) technique. Brewster Angle Microscopy was utilized to investigate the Langmuir monolayer formation at the air-water interface. The morphology and thickness of the films were studied using SEM, White Light, Raman and optical microscopies. The charge transport properties of N-GNPs LS films were investigated using cyclic voltammetry and Electrochemiluminescence (ECL). The as-prepared N-GNPs LS films revealed interesting morphological features and peculiar charge transport properties. The films were used for the detection of different analytes, such as dopamine, caffeine and omeprazole. These studies revealed that the introduction of graphene into Nafion LS films not only facilities the electron transfer, but also improves the long- term stability of the sensor. The N-GNPs LS films were used for ECL detection of tripropylamine with the luminophore $[Ru(bpy)_3]^{2+}$ incorporated in the N-GNPs dispersion during the LS fabrication. The ECL detection of dopamine was also investigated. ECL appears promising for detection of trace of analytes of forensic and pharmaceutical interest.

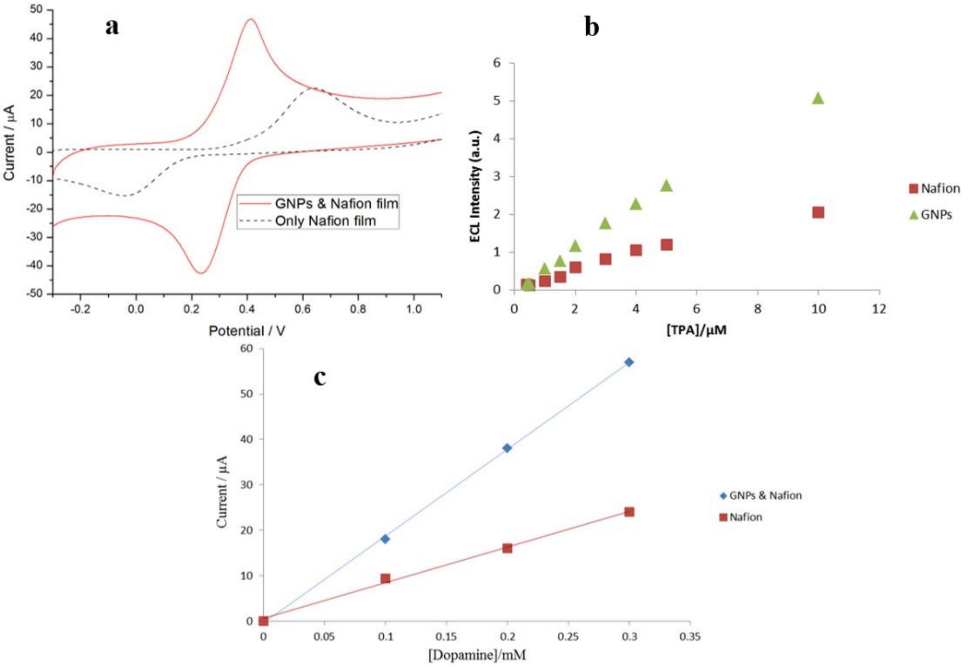


Figure 1. (a) CV of a 10-layers LS films with 0.2mM Dopamine recorded in 0.1 M NaCl as supporting electrolyte; scan rate of 0.1 Vs^{-1} (b) ECL of a 10-layers LS–$[Ru(bpy)_3]^{2+}$ films with increasing concentration of TPA recorded in 25 mM Borax buffer pH 7.5 as supporting electrolyte; scan rate of 0.1 Vs^{-1} and (c) CV of a 10-layers LS films with increasing concentration of Dopamine recorded in 0.1 M NaCl as supporting electrolyte; scan rate of 0.1 Vs^{-1}

P15.

Gold Nanoparticles Covered with C_{70} Fullerene Derivative as a Promising Platform for Immobilization of NAD-dependent Glucose Dehydrogenase

Katarzyna Jakubow, Piotr Piotrowski, Andrzej Kaim, Barbara Kowalewska

Department of Chemistry, University of Warsaw,
Pasteura 1, PL-02-093 Warsaw, Poland
kjakubow@chem.uw.edu.pl

Fullerenes have been widely studied due to their interesting electronic, structural and spectroscopic properties.[1] For this reason they have attracted much attention as novel carbon materials for sensors.[1,2] C_{70} fullerene as an electron acceptor displays exceptional electrochemical behavior due to its remarkable electronic and dimensional structures. As a result, it can facilitate the electron transfer between the active site of the enzyme and the electrode surface. These unique properties of fullerenes and their derivatives provide therefore a suitable micro-environment for enzymes immobilization, simultaneously maintaining their biological activity. Gold nanoparticles (AuNPs) are also considered as a promising platform for enzymatic biosensors, due to their size dependent electronic properties,[3] high active surface area,[4] biocompatibility[5]and stability of their composite materials.

In presented work, to facilitate the electron transfer between enzyme molecule and electrode surface, AuNPs covered with C_{70} fullerene derivative were employed. Combination of those two components along with glucose dehydrogenase (GDH) enzyme lead to the formation of integrated bio-electrocatalytic system for effective oxidation of glucose. GDH catalyzes the oxidation of D-glucose to gluconolactone in the presence of coenzyme NAD^+ (nicotinamide adenine dinucleotide), which is reduced to NADH.[6] In order to achieve the sufficient transfer of electrons from biomolecule to the electrode surface, NADH have to be regenerated at the suitable potential at the nanomaterial modified electrode surface. Resulting novel electrochemical glucose biosensor exhibited high sensitivity (26.1 μA mM^{-1} cm^{-2}) and wide linear range (0.25-12.0 mM). The apparent Michaelis-Menten constant was calculated by the electrochemical version of the Lineweaver-Burk plot and was found to be K_M=24.1 mM specifying enzymatic activity and affinity of immobilized enzyme towards glucose. Moreover, our device was characterized by stable, rapid response implying that it can be used for quantitative detection of glucose in real samples. These properties suggest that the prepared hybrid nanocomposite is very promising to find potential application as a dioxygen insensitive biosensor.

References

1. R. Dagani *Chem. Eng. News* **2002**, *80*, 32.
2. J. A. Rather, K. De Wael *Sens. Actuators, B* **2013**, *176*, 110.
3. R. N. Goyal, V. K. Gupta, N. Bachheti *Anal. Chim. Acta* **2007**, *597*, 82.
4. T.A. El-Brolossy, T. Abdallah, M.B. Mohamed, S. Abdallah, K. Easawi, S. Negm and H. Talaat *Eur. Phys. J. Special Topics.* **2008**, *153*, 361.
5. Y.-C. Yeh, B. Creran and V.M. Rotello *Nanoscale* **2012**, *4*, 1871.
6. I. Fratoddi, I. Venditti, C. Cametti and M.V. Russo *J. Mater. Chem. B* **2014**, *2*, 4204.
7. T. Hoshino, S. Sekiguchi, H. Muguruma *Bioelectrochem.* **2012**, *84*, 1.

P16. Electrochemical Bioimprinted Detection of Butyl Paraben on a Modified Carbon Paste Electrode with Safranine Capped with Silver Nanoparticles

Sophia Karastogianni, Stella Girousi

Aristotle University of Thessaloniki, Analytical Chemistry Laboratory,
Chemistry Department, Greece
skarastogianni@hotmail.com

The aim of the present study is the development of novel, sensitive, selective, environmentally friendly and also cost effective molecular imprinted polymers (MIP) electrochemical sensors for the determination of butyl paraben. Thus, AgNPs were synthesized under the effect of solar light. Quantity of $AgNO_3$ and safranine (Sa) was mixed and dispersed in NaOH solution. The final solution was stirred for 5 minutes thinly. Then, this solution was exposed in the solar light in static condition and a colour change was observed. The resultant reaction mixture was then kept at normal room condition and washed with water and ethanol and dried in vacuum desiccator. Afterwards, silver nanoparticles capped with safranine (AgNPs@Sa) were studied with ultraviolet - visible spectroscopy (UV-Vis) and infrared spectroscopy (IR). The morphology of AgNPs@Sa was studied with scanning electron microscopy (SEM). AgNPs@Sa were electrochemically studied with cyclic voltammetry (CV) and square wave voltammetry (SWV) on a carbon paste electrode (CPE). Following these procedures, the novel bioimprinted biosensor was developed. Firstly, the interaction between butyl paraben and AgNPs@Sa in solution phase was carried out in an appropriate buffer solution containing salt, butyl paraben DNA and AgNPs@Sa and the mixture was stirred for the appropriate time. The, cyclic voltammetric electrodeposition was performed in imprinted solution for the fabrication of bioimprinted sensor. As a control electrode, the non-bioimprinted polymer (NBIP) electrode was prepared under the same experimental procedure without adding butyl paraben. Then, the electrode was dried at room temperature. After that, the modified electrode was immersed in an ethanol: acetic acid (80:20) solution to remove the template from the polymer. For comparison, an AgNPs@Sa imprinted electrode (as described above except that no DNA was used) and a DNA biosensor were prepared. For electrochemical measurement, butyl paraben was firstly accumulated on the sensor surface. The electrochemical performance of the bioimprinted sensor was characterized by different techniques including CV and SWV. The CV measurements were performed in $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ and KCl as a probe solution. The same probe solution was used for SWV experiments. The bioimprinted sensor was evaluated under optimum condition to confirm its electrochemical properties such as linearity, selectivity, stability and reproducibility. Moreover, it was applied for the analysis of butyl paraben in real samples. To the best of our knowledge, it is the first detection effort to analyze butyl paraben with the combination of MIP electrochemical sensors and natural dyes as well as AgNPs as electrode surface modifiers. Furthermore, to our best knowledge, no such reports were found for the synthesis of Sa-capped silver nanoparticles by adopting this green method. Furthermore, the AgNPs@Sa modified on CPE (AgNPs@Sa/CPE) was employed for the electrochemical detection of butyl paraben.

Acknowledgements

The present study was financed from “IKY FELLOWSHIPS OF EXCELLENCE FOR POSTGRADUATE STUDIES IN GREECE-SIEMENS PROGRAM”

P17. How to Prepare a Biomimetic Model of the Outer Membrane of Cell Membrane of Gram-negative Bacteria

Bishoy Khairalla,[a] Izabella Brand,[a] Slawomir Sek[b]

[a] *Department of Chemistry, Carl con Ossietzky university of Oldenburg,*
D-26111 Oldenburg, Germany.
[b] *Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw,*
Zwirki i Wgury 101,02-089 Warsaw, Poland.
bishoy.khairalla@uni-oldenburg.de

Biological cell membranes are composed of a fluid lipid bilayer matrix, which hosts a large variety of proteins. Symmetric phospholipid bilayers (e.g. phosphatidylcholine) are good models of cell membranes of eukaryote. The cell membrane of gram-negative bacteria has a distinct composition and structure. The cell membrane of gram-negative bacteria is composed of two lipid bilayers: the inner membrane (IM) contacting plasma and an outer membrane (OM) having a direct contact with the outside environment. Both membranes are separated by 8 nm thick periplasm layer. The OM is asymmetric. The inner leaflet contains phospholipids, while the outer leaflet is composed of lipopolysaccharides. The OM of gram-negative bacteria is exposed for interactions with the environment and seems to play an important role in the action of antimicrobial peptides with bacteria.

A fabrication of realistic asymmetric and stable models of OM of gram-negative bacteria is of crucial role to understand their interactions with antimicrobial peptides. In this work asymmetric lipid bilayers are prepared on a gold surface. The inner leaflet is composed of phosphatidylethanolamine and the outer leaflet from phosphoglycerol. Lipids containing saturated and unsaturated hydrocarbon chains are used. The influence of divalent metal cations on the hydration and integrity of the fabricated asymmetric bilayer is taken into account. Langmuir-Blodgett combined with Langmuir Schaefer transfer (LB-LS) are used to prepare lipid bilayers on gold surface. The LB-LS transfer offers control of the lateral packing of lipid molecules in the model membrane. Before the transfer onto a solid substrate, a lipid monolayer at the air/water interface is compressed to a selected surface pressure. The transfer of lipid monolayers is performed at $25 < \Pi < 42$ mN m^{-1} in order to mimic the packing, orientation and physical sate of biological cell membranes.

Surface characterizing techniques such as polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) and atomic force microscopy (AFM), both with electrochemical control are used to characterize the structure, physical state, hydration, thickness and morphology of the asymmetric bilayers.

P18. Self-assembled Functionalized Thiols Monolayers for Capacitive Sensing of Potassium Ions Based on Electrostriction Phenomenon

Maria Madej, Marcin Wieczorek, Karolina Starzec, Paweł Knihnicki,
Paweł Kościelniak, Jolanta Kochana

*Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University,
Gronostajowa 2, 30-387 Krakow, Poland*

The electrostriction phenomenon, described in literature in 1960's,[1] is defined as a change of dimensions of materials under the influence of an electric field. The phenomenon can be noticed for self-assembled monolayers (SAMs) supported on an electrode surface and could be employed for electrochemical detection of electrochemically-inactive substances, which are not susceptible to redox processes.[2]

The aim of the work was to develop capacitive sensor based on the electrostriction phenomenon of SAMs of a thiol supported on the surface of a gold electrode. The gold electrode covered by long-chain functionalized thiols can be considered as a capacitor whose covers are the electrode surface from one side, and an electrolyte solution from the other side. Several types of interaction between functional groups of SAMs and components of the electrolyte can be noticed: adsorption, association, forming of hydrogen or coordination bonds, redox reaction or antigen-antibody interactions.[3] The interactions between an analyte and the thiol affect capacitance-potential characteristics, and these changes are proportional to the analyte concentration.

A capacitive sensor for determination of potassium ion is proposed. For sensor development crown ether with the chain ended with the thiol group (18-crown-6 thiol ether) was synthesized and procedures of the gold electrode surface preparation and thiol layers formation were elaborated. The characteristic curves, a capacitance as a function of potential, were recorded in solution of different analyte concentrations. As an analytical signal the value of capacitance for the selected potential was used. The employing of chemical H-point standard additions calibration method (C-HPSAM) allowed to determine potassium ion in mineral waters (even highly mineralized) and vegetable juices with satisfactory accuracy (relative error ca. 5-7%) and very good precision (less than 5%). No need to use additional steps to eliminate the interference effects caused by unknown and very complex samples matrices fits in the principles of green analytical chemistry.

Acknowledgments

The study was supported by the National Science Centre, Poland, Project 2013/11/B/ST4/00864.

References

1. V. Babakov, L. N. Ermishkin, E. A. Lieberman *Nature* **1966**, *210*, 953.
2. T. Hianik *Rev. Mol. Biotechnol.* **2000**, *74*, 189.
3. S. Kalinowski, Eletrochemical methods and their application, in: A. Ottava (Ed.), *Advances in Planar Lipid Bilayers and Liposomes*, 2, Elsevier Inc., **2005**, pp. 1-49.

P19. Conformational Changes in Bovine Serum Albumin Self-assembled Monolayers

P. Komorek,[a] I. Brand,[b] B. Jachimska[a]

[a] *J. Haber Institute of Catalysis and Surface Chemistry, Cracow, Poland*
[b] *Department of Chemistry, Carl von Ossietzky University of Oldenburg, Oldenburg, Germany*
paulina-komorek@wp.pl

Biopolymers are characterized by a wide range of properties, which allow us to use them in many areas of life sciences such as medicine, pharmacy or cosmetic industry. Proteins are biopolymers which find numerous applications in biotechnology. When a protein is exposed to a solid material it adsorbs on its surface. This common phenomenon is, however, very complex. The adsorption of proteins into solid surfaces may lead to changes in their conformation and secondary structure comparing to the situation in a liquid phase. Obviously, these changes may affect the protein reactivity and biological functions. Therefore studies aiming at understanding of the relationship between the structure and activity of adsorbed proteins are highly required.

In this research a model protein: bovine serum albumin (BSA) was adsorbed on the gold surface. The process of adsorption was studied as a function of different environmental conditions: electrolyte composition, pH, ionic strength and time of adsorption. Multi-parametric surface plasmon resonance (MP-SPR), atomic force microscope (AFM), dynamic light scattering (DLS) and computer modeling (MD) allowed for the determination of the orientation of the films formed by the adsorbed protein. A combination of quartz crystal microbalance with dissipation monitoring (QCM-D) and MP-SPR complementary techniques has provided crucial information on hydration of monolayers.

The secondary structure of the adsorbed protein was determined using polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). It allowed for investigating the stability of secondary structure of BSA in different conditions (pH, protein concentration and time of adsorption).

P20. Modified Cyclodextrins as Carriers of Drug Molecules Containing an Anthraquinone Moiety

A. Krzak,[a] M. Majdecki,[b] O. Swiech,[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

Cyclodextrins (CDs) are cyclic oligosaccharides composed of D-glucopyranoside units linked by glycosidic bonds. Their spatial structure resembles the shape of a truncated cone with a hydrophobic inner cavity and hydrophilic outer surface. CDs are able to form host-guest inclusion complexes with a hydrophobic molecules as a guest. These noncovalent inclusion complexes offer a variety of advantages over noncomplexed forms of a drug. Cyclodextrins are primarily used to enhance the aqueous solubility, physical chemical stability, and bioavailability of drugs. Their other applications include preventing drug–drug interactions, converting liquid drugs into microcrystalline powders, reducing or eliminating unpleasant taste and smell.[1,2] In our study, drugs containing anthraquinone moiety: 9,10-anthraquinone sulfonic and carboxylic acids (AQ2S, AQ2CA) are the guest molecules in the cyclodextrin host-guest type of complexes. Native cyclodextrin complexes have the disadvantage of low stability constants, however modification of CD with appropriate aromatic groups can increase the stability constants of the CD-drug complex.[3]

Compounds with the anthraquinone moiety are often employed in medicine. AQ2S is a neuroprotective agent, while AQ2CA is used in the relief or prophylaxis of allergic condition. However, these drugs are characterized by low solubility in aqueous solutions which seriously limits their applicability.[4]

Another factor limiting the full use of the anthraquinone derivatives is their ability to generate reactive oxygen species (ROS) affecting also the healthy cells. The formation of strong inclusion complexes between the anthraquinone derivatives and cyclodextrins would reduce the unwanted side effects and improve the drug solubility.

The aim of this study was to investigate the electrochemical and spectroscopic behaviour of the complexes formed between newly synthesized βCD derivatives and the selected drugs containing 9,10-anthraquinone moieties. We determined the drug solubility in the presence of cyclodextrin, and using the modified Osa equation - the stability constants of these complexes in physiological pH, 7.4, and at more acidic pH typical for cancer affected environment.

References

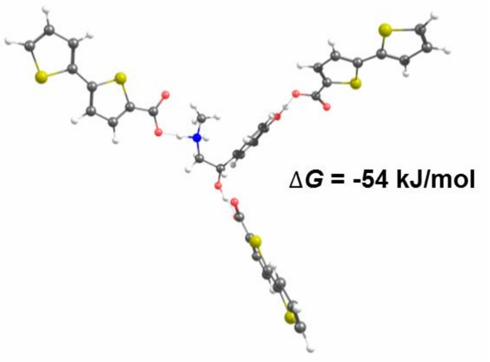
1. E. M. M. Del Valle *Process Biochem.* **2004**, *39*, 1033.
2. R. Arun, K. C. K. Ashok, V. V. N. S. S. Sravanthi *Sci. Pharm.* **2008**, *76*, 567.
3. O. Swiech, A. Mieczkowska, K. Chmurski, R. Bilewicz *J. Phys. Chem. B* **2012**, *116*, 1765.
4. S. Y. Tsai, S. C. Kuo, S. Y. Lin *J. Pharm. Sci.* **1993**, *82*, 1250.

P21. Self-reporting Molecularly Imprinted Polymer for Label-free Selective Electrochemical Sensing of *p*-Synephrine

Patrycja Lach,[a] Maciej Cieplak,[a] Piyush Sindhu Sharma,[a] Marta Sosnowska,[a] Krzysztof Noworyta,[a] Francis D'Souza,[b]* and Wlodzimierz Kutner[a,c]**

[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, Woycickiego 1/3, 01-815 Warsaw, Poland

Molecularly imprinted polymers (MIPs) are excellent example of bio-mimicking recognition materials.[1] They have found numerous applications in selective chemosensing. For electrochemical determination of electroinactive analytes, usually some external redox probe is added to the sample solutions. It is assumed that binding of target analyte molecules by MIP molecular cavities causes MIP film swelling or shrinking. This behavior leads to changes in MIP film permittivity for the redox probe and thus changes in faradaic currents corresponding to reduction or oxidation of the redox probe (so called “gating effect”) in CV and DPV determinations.[2,3] However, electrochemical impedance spectroscopy spectra recorded in our previous research[4] allow us to speculate that diffusion of a redox probe is a not crucial issue in terms of selective determination with the MIP film coated electrode. Therefore, a new specially designed monomer, vis., *p*-*bis*(2,2'-bithien-5-yl)methyl-ferrocene benzene was used for deposition of a self-reporting MIP film. This monomer acted as both a crosslinking monomer and an internal redox probe. It was electropolymerized together with 2,2'-bitiofen-5-carboxylic acid in the presence of the *p*-synephrine template – a diet supplement that is suspected of causing serious cardiovascular diseases. These self-reporting MIP film modified electrodes were used for electrochemical determination of *p*-synephrine in the absence of the external redox probe. The DPV measurements using PBS (pH = 7.4) showed oxidation of ferrocene at ~450 mV vs. Ag/AgCl and a relative change of the DPV peak current was proportional to the concentration of *p*-synephrine in the range of 10 to 100 nM with the LOD equal to 5 nM.



Scheme 1. B3LYP 3-21g DFT optimized structure of pre-polymerization complex of the *p*-synephrine molecule with three molecules of functional monomers.

References

1. M. Cieplak, W. Kutner *Trends Biotechnol.* **2016**, *34*, 922.
2. Y. Yoshimi, R. Yoshiizumi, R. Arai, I. Nakano, S. Sekine *J. Chem. Eng. Japan* **2009**, *42*, 600.
3. Y. Yoshimi, K. Sato, M. Ohshima, E. Piletska *Analyst* **2013**, *138*, 5121.
4. T. P. Huynh, K.C.C. Bikram, W. Lisowski, F. D'Souza, W. Kutner, *Bioelectrochemistry* **2013**, *93*, 37.

P22. Electropolymerized Molecularly Imprinted Polymers for the Detection of Hazardous Substances Through Electrochemical Sensing

Nadja Leibl, Carlo Gonzato, Karsten Haupt

Université de Technologie de Compiègne, Compiègne, France
nadja.leibl@utc.fr

Molecular imprinting is established as one of the most versatile techniques to generate synthetic receptors with specific molecular recognition properties for target molecules. Molecularly imprinted polymers (MIPs) are stable, tailor-made synthetic materials with binding affinities and selectivity comparable to those of antibodies, hormone receptors and enzymes[1]. They are used in many fields, such as bioimaging[2], purification[3], chemical sensors including chemical sensors for hazardous materials[4].

Various methods have been used to interface MIPs with transducer surfaces including drop-coating of a polymer solution, covalent immobilization of MIPs, in-situ polymerization or spin coating of MIPs and electro polymerization of electroactive monomers.[5] Films resulting from electro polymerization have been found to be superior to conventional MIPs nanoparticles, thanks to their stable attachment to the transducer, their ease synthesis in aqueous/non-aqueous solutions and an easier pathway for conduction of electrons across the electrodes.

The possibility of carefully tuning hydrophobicity, biocompatibility, and film thickness make MIP films a prominent material for sensors.

This work describes the development of an electropolymerized MIP films for sensing 2,4,6-trinitrolutene (TNT) and its analogues. As polymer matrix, a non-conductive, hydrophilic polydopamine film was synthesized by cyclic voltammetry with tunable thickness[6] for electrochemical sensing.

References

1. S. A. Piletsky, E. V. Piletska, A. Bossi, K. Karim, P. Lowe, A. P. F. Turner *Biosens. Bioelectron.* **2001**, *9-12*, 701.
2. M. Panagiotopoulou, Y. Salinsas, S. Beyazit, S. Kunath, L. Duma, E. Prost, A. G. Mayes, M. Resmini, B. Tse Sum Bui and K. Haupt *Angew. Chem. Int. Ed.* **2016**, *55*, 8244.
3. S. Nesora, F. Merlier, E. Prost, K. Haupt, C. Rossi and B. Tse Sum Bui *J. Chromatogr. A* **2016**, *1465*, 47.
4. W. Lu, M. Xue, Z. Xu, X. Dong, F. Xue, F. Wang, Q. Wang and Z. Meng *Curr. Org. Chem.* **2015**, *191*, 62.
5. M. C. Blanco-López, S. Gutiérrez-Fernández, M. J. Lobo-Castañón, A. J. Miranda-Ordieres and P. Tuñón-Blanco *Anal. Bioanal. Chem.* **2003**, *378*, 1922.
6. B. Stöckle, D. Y. W. Ng, C. Meier, T. Paust, F. Bischoff, T. Diemant, R. J. Behm, K.-E. Gottschalk, U. Ziener, T. Weil *Macromol. Symp.* **2014**, *346*, 73.

P23. Nanomechanical Characterization of Biomimetic Membrane after Antimicrobial Peptide Adsorption Studied with Peak Force QNM Atomic Force Microscopy Mode

Marta Majewska, Piotr Pieta

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

Understanding interactions between biologically active compounds, such as antimicrobial agents or pharmaceuticals, and model biological membranes are of high interest due to usefulness in designing new kinds of drugs, including antibiotics. Mechanism of action of antimicrobial peptides is not yet well understood. In this study, we observed interactions between newly synthesized bacteriocin, BacSp222[1], with biomimetic membrane. Such model biological membrane comprised of 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) phospholipid bilayer was deposited on an atomically flat mica surface in the presence of 10 mM HEPES, 150 mM NaCl, 5 mM $CaCl_2$, pH 7.4 buffer. Atomic force microscopy (AFM) was used to image phospholipid bilayer before and after adsorption of BacSp222 molecules. We have observed formation of transmembrane pores due to peptide activity. Detailed analysis of force curves collected with the use of PeakForce QNM mode allowed to analyze changes in nanomechanical properties of the membrane surface, such as Young's modulus, deformation, adhesion and dissipation. Obtained results correspond well with PM-IRRAS study of interaction between the peptide and the DMPC bilayer[2], which showed the peptide is biologically active and disrupts the membrane according to the barrel-stave model.

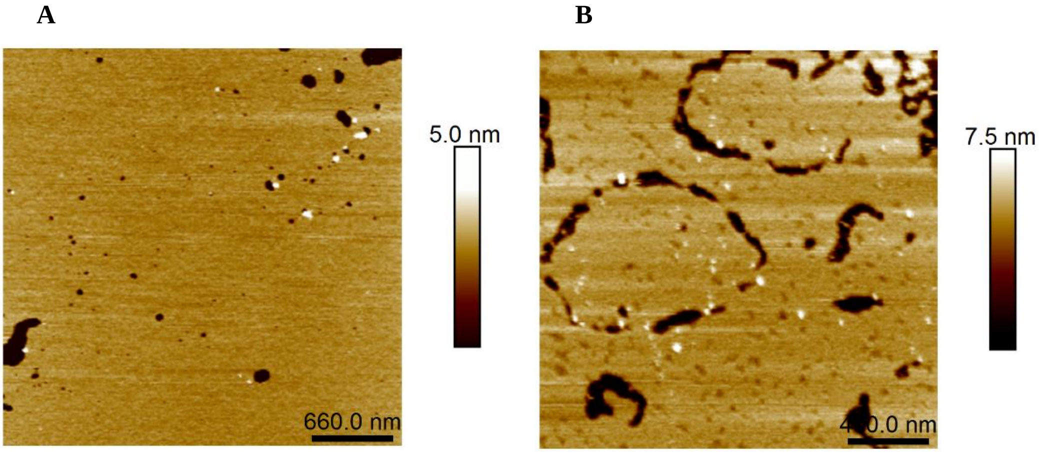


Figure 1. (A) Uniform DMPC bilayer with normally occurring defects visible, (B) DMPC bilayer after antimicrobial peptide adsorption.

References

1. B. Wladyka, M. Piejko, M. Bzowska, P. Pieta, M. Krzysik, Ł. Mazurek, I. Guevara-Lora, M. Bukowski, A. J. Sabat, A. W. Friedrich, E. Bonar, J. Międzobrodzki, A. Dubin, P. Mak *Sci. Rep.* **2015**, *5*, 14569.
2. P. Pieta, M. Majewska, Z. Su, M. Grossutti, B. Wladyka, M. Piejko, J. Lipkowski, P. Mak *Langmuir* **2016**, *32*, 5653.

P24.

Development of an Electrochemical Chemosensor for Asymmetric Dimethylargininie Detection with Molecularly Imprinted Recognition Layer

Valerii Malyshev,[a] Raghu Chitta,[b] Francis D`Souza,[c] Krzysztof Noworyta[a]

[a] *Institute of Physical Chemistry Polish Academy of Science, Warsaw, Poland*
[b] *Department of Chemistry, Central University of Rajasthan, Rajasthan, India*
[c] *Department of Chemistry, University of North Texas, Denton TX, USA*
vmalyshev@ichf.edu.pl

Early diagnosis of renal diseases play a key role in their effective treatment. Biomarkers present in body fluids, which are currently used for diagnosis of this illness, are strongly affected by different non-renal factors (e.g. patient gender, age, diet etc.). Consequently, searching for new biomarkers, and methods of their determination, continued to be a very important. One of such promising biomarkers of renal dysfunctions is asymmetric dymethyl arginine (ADMA)[1] as its normal concentration level in blood serum is independent of age, gender, and diet. The main goal of this work was to develop a chemical sensor with molecularly imprinted polymer (MIP) layer as recognition unit for selective determination of ADMA. To develop the ADMA-imprinted polymer, benzoic acid and 18-crown-6-appended bis(bithienyl)methane derivatives were used as functional monomers. Structure of pre-polymerization complex of ADMA with these monomers was optimized with *Gaussian 09* software using the B3LYP/6-31G functional and basis set. These calculations indicated formation of a stable complex with ΔG of -499 kJ/mol. The MIP and NIP films were deposited on Pt disk electrode by electrochemical polymerization in potentiodynamic conditions. Extraction of template was proved by differential pulse voltammetry (DPV) and Surface Enhanced Raman Spectroscopy (SERS). Subsequently, behavior of the devised chemosensor was tested by using DPV and electrochemical impedance spectroscopy (EIS) as transduction techniques. The sensor showed sensitivity reaching about 1.98×10^{-2} µA/µM and limit of detection of 0.3 µM when DPV was used as transduction technique, while impedimetric sensor exhibited sensitivity of 86.1 Ω/µM and limit of detection 0.4 µM. This ADMA chemosensor was also found to work in the presence of large excess of interfering compounds indicating its potential use in *in-vivo* and *in-vitro* monitoring of ADMA. In order to increase accessibility of imprinted cavities use of the sacrificing layer of Metal-Organic Framework (MOF) crystals has been attempted.

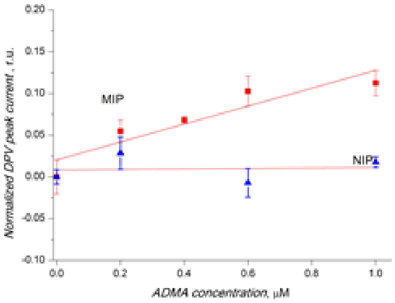


Figure 1. Calibration plot for MIP and NIP coated electrode with DPV as transduction technique.

Acknowledgements
This work was partially supported by the Polish National Science Centre grant No. 2014/15/B/ST4/04642.

References

1. C. Fleck, F. Schweitzer, E. Karge, M. Busch, G. Stein *Clin. Chim. Acta* **2003,** *336,* 1.

P25.

Monoolein Cubosomes Doped with Magnetic Nanoparticles – a Hybrid Material for Drug Release

Monika Mierzwa, Paweł Krysiński, Renata Bilewicz

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

Lipidic liquid crystal materials can be prepared in the form of cubic phase or cubosomes - dispersed LCP into nanoparticles. Both forms have the same properties which make them highly interesting as the matrix for drug delivery - they are non-toxic, bioadhesive, biodegradable in the body and have a large inner surface and can accommodate the appropriate amount of active molecules of any polarity. But cubosomes have an advantage over cubic phase because they have lower density. Cubosomes doped with nanoparticles are of interest as the drug delivery systems and as contrast agents for magnetic resonance imaging (MRI).[1,2]

We prepared hybrid cubosome dispersions – magnetocubosomes, loaded with magnetic NPs and drug. The TEM and Cryo-SEM images shows the spherical morphology of the cubosomes and confirmed that the nanoparticles are inside the cubosomes. The size of the LCP particles was obtained from the analysis of DLS measurements. The cubic nature of the LCP dispersion was characterized by SAXS. The drug release profiles from the magnetocubosomes were established using SWV. The experiments were performed in the absence/presence of external magnetic field. We received LCP nanoparticles with average diameter of 150nm and $Im\bar{3}m$ cubic structure, which exhibit magnetic properties allows to move in a magnetic field. We also show that the use of the magnetic field accelerates the elution of the drug.

Acknowledgements
The financial support of Sinergia project no. CRSII2_154451/1 “Design, synthesis and characterization of lipidic nanomaterials for biomedical and biosensing applications”.

References

1. M. Szlezak, D. Nieciecka, A. Joniec *et al. ACS Appl. Mater. Interfaces*, **2017**, *9*, 2796.
2. D. P. Acharya, B. A. Moffat, A. Polyzos *RSC Adv.* **2012**, *2*, 6655.

P26.

Mesoporous Silica Thin Films for Improved Electrochemical Detection of Paraquat

T. Nasir, G. Herzog, A. Walcarius

Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), UMR 7564,
CNRS-Université de Lorraine. 405, rue de Vandoeuvre 54601 Villers-lès-Nancy, France
tauqir.nasir@univ-lorraine.fr

Mesoporous silica film modified electrodes have gained much importance recently in the field of electrochemistry and sensing.[1] In this study we used glassy carbon electrodes (GCE) previously modified by electrografting 3-aminopropyltriethoxysilane (APTES) and followed by mesoporous silica thin film deposition using electro-assisted self-assembly (EASA) method.[2] APTES modification is proved to increase the adhesion of silica thin films onto glassy carbon electrodes,[3] which is of major importance when it comes to using silica thin film modified GCE for electroanalytical applications.

Paraquat (1, 1-dimethyl-4, 4-bipyridinium dichloride) also known as methylviologen is non-selective, contact herbicide being used in agricultural practices to control broad leaf weeds since 1960's. Paraquat is soluble in water, highly toxic for living organisms (LD_{50} for humans 40-60 mg / kg) and has caused thousands of deaths in last few decades[3]. It causes serious damage to liver, lungs, heart, kidneys and is involved in the development of Parkinson's disease; it is banned in the European Union but still widely used in more than 100 countries.[4]

Square wave voltammetry (SWV) was used for the electrochemical detection of paraquat at mesoporous silica modified GCE and unmodified GCE. Effect of various parameters (solution pH, ionic strength and nature of electrolyte) on sensitivity and electrochemical signal was studied. As mesochannels of negatively charged silica surface and debye length both are in nanometer scale, which favours the mass transport and accumulation of positively charged paraquat into the film matrix resulting in enhanced electrochemical signal and sensitivity (almost 30x higher) at silica modified electrode as compared to the unmodified one. Calibration plot for 10-50 nM paraquat at modified GCE were linear, limits of detection and quantification by this method were found to be 4 and 13 nM, respectively. Calibration plots for paraquat were also established by using aqueous real samples.

References

1. A. Walcarius *Electroanalysis* **2015**, *27*, 1303.
2. A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja *Nat. Mater.* **2007**, *6*, 602.
3. T. Nasir, L. Zhang, N. Vilà, G. Herzog, A.Walcarius *Langmuir* **2016**, *32*, 4323.
4. M. Watts, *Paraquat Monograph*. Pesticide Action Network Asia & the Pacific (PAN AP), **2011**.

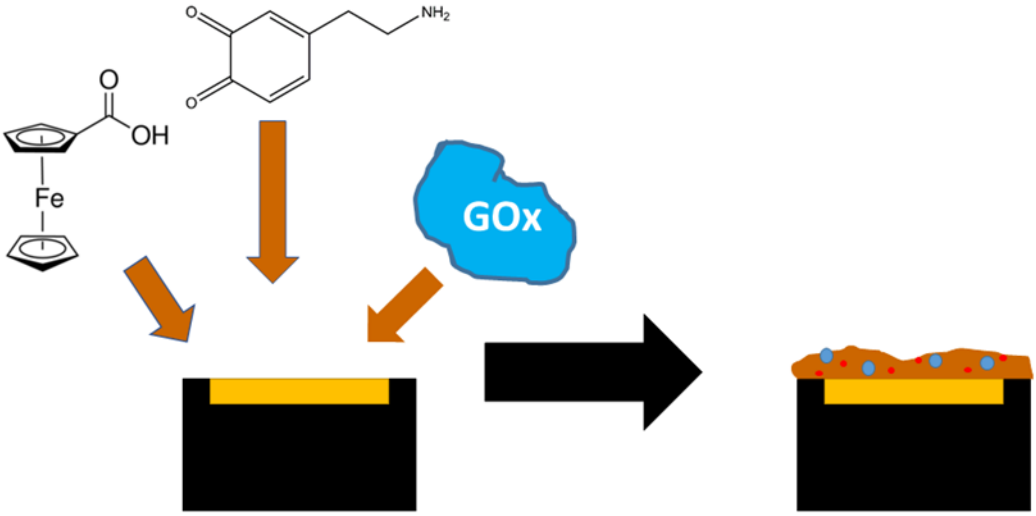
P27. Development of Polydopamine Modified Surfaces for Glucose Amperometric Biosensors

Roberto Ortiz, Esben Thormann

Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark
Robor@kemi.dtu.dk

Since its description for 10 years ago, films formed by the polymer produced by the self-polymerization of dopamine (DA) has been applied in a wide range of applications across the chemical, biological, medical, and materials sciences.[1] Its facile preparation method, high adhesive properties, presence of quinones in the films and easy post-modification make it an appropriate material for electrochemical methods. Unfortunately, its full development for energy storage systems and electrochemical sensors has been hindered by the low conductivity of the films formed and the insulation properties of PDA thick films.

As a proof-of-concept approach, ferrocene and glucose oxidase are co-immobilized onto gold electrode with polydopamine forming films by polymerization of dopamine. The method developed is applicable in virtually any electrode or surface. The prepared films and polymers are characterized using AFM, QCM-D and electrochemical methods. The preparation of the sensor, limit of detection and calibration curve and sensitivity is presented.



References

1. H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith *Science* **2007**, *318*, 426.

P28. Synthesis and Characterization of Holmium-Doped Iron Oxide Superparamagnetic Nanoparticles

Magdalena Osial, Paweł Krysiński

Laboratory of Electrochemistry, Faculty of Chemistry, University of Warsaw
magdalena@osial.eu

Recent development of medical diagnostic techniques requires novel approach in targeted anticancer therapies. Within our work we focused on the synthesis and characterization of superparamagnetic iron oxide-based nanoparticles SPIONs doped with holmium as the core of radionuclides dedicated for hyperthermia of the tumor tissues. SPIONs were obtained through the coprecipitation and solvothermal technique from solutions containing the source of iron and holmium ions. During the synthesis part of iron (III) ions are replaced by holmium and built-up into the crystallographic lattice. Due to the changes in the physico-chemical properties after changing the holmium concentration in the synthesis bath and temperature during synthesis the structural and morphologic analyses were performed.

Acknowledgements
This project was supported by the National Science Centre - grant no. UMO-2016/21/B/ST4/02133.

References

1. K. Maier-Hauff, F. Ulrich, D. Nestler, H. Niehoff, P. Wust, B. Thiesen, H. Orawa, V. Budach, A. Jordan *J Neurooncol.* **2011,** *103*, 317.
2. P. Kaur, M. D. Hurwitz, S. Krishnan, A. Asea *Cancers* **2011**, *3*, 3799.
3. K. Turcheniuk, A.V. Tarasevych, V.P. Kukhar, R. Boukherroub, S. Szunerits *Nanoscale*, **2013**, *5*, 10729.

P29. Electrochemical Sensor Based on Titania Dioxide Sol Modified with Mesoporous Carbon Enriched with Gold Nanoparticles for Sensitive Determination of β-lactam Antibiotic

Aleksandra Pollap, Paulina Gąsior, Jolanta Kochana

Department of Analytical Chemistry, Faculty of Chemistry,
Jagiellonian University in Krakow, Krakow, Poland
aleksandra.pollap@doctoral.uj.edu.pl

Significant increase of environmental pollution including environmental water by various substances, especially pharmaceutical preparations, leads to searching for newer and better methods of their identification and detection.[1]

This work is devoted to the development of a new electrochemical sensor for the determination of the antibiotic from the β-lactam group – amoxicillin. The construction of developed sensor was based on modifying the graphite electrode with the use of titania dioxide sol modified with mesoporous carbon CMK-3 enriched with gold nanoparticles which application significantly increased the sensitivity of proposed sensor. The composition of the nanocomposite was supplemented with conductive polymer - Nafion.

After the optimization of measurement conditions the developed sensor was characterized by linear range, sensitivity, limit of detection and long-term stability. Sensor based on TiO_2 sol enriched with mesoporous carbon CMK-3, gold nanoparticles and Nafion exhibits good analytical parameters including wide linear range (2.1 - 133.0 μM) and high sensitivity (832 μA mM^{-1}). Additionally, the analysis of real samples for amoxicillin content displayed that developed sensor could be successfully applied for the determination of amoxicillin in environmental water.

References

1 A. Perez-Parada, A. Aguera, M. del Mar Gomez-Ramos, J. F. Garcia-Reyes, H. Heinzen, A. R. Fernandez-Alba *Rapid Commun. Mass Spectrom.* **2011**, *25*, 731.

P30. Lipid Bilayers Cushioned with Polyelectrolyte-based Films on Doped Silicon Surfaces

Lukasz Poltorak,[a] Mark L. Verheijden,[b] Duco Bosma,[a] Pascal Jonkheijm,[b]
Louis C. P. M. de Smet,[a,c] Ernst J. R. Sudhölter[a]

[a] *Delft University of Technology, Department of Chemical Engineering, Delft, The Netherlands*
[b] *Molecular Nanofabrication Group of the MESA+*
Institute for Nanotechnology and Bioinspired Molecular Engineering,
Laboratory of the MIRA Institute for Biomedical Technology and Technical Medicine, Department of Science and Technology, University of Twente, Enschede, The Netherlands
[c] *Wageningen University & Research, Laboratory of Organic Chemistry,*
Wageningen, The Netherlands
l.poltorak@tudelft.nl

Platforms bridging electronic devices with biological systems attract considerable attention due to their relevance in number of applications, including drug screening, electroanalytical sensing, risk evaluation or bioinspired energy conversion. Silicon semiconductors, among other transducing electronic components, are materials with a well-understood and optimized manufacturing process that allows miniaturization down to nanometer level.[1] Moreover, the chemistry of (oxidized) silicon enables straightforward functionalization leading to desired and adjustable surface properties.[2] Both aspects are essential from the electroanalytical point of view since miniaturization leads to higher mass transport (higher sensitivity) and increases the signal-to-noise ratio. On the other hand, surface functionalization allows a design of the surface properties in such a way that the sensor becomes specific towards particular analytes or/and allows the adjustment of a surface physicochemical properties.

In this work, we study the electrical properties of sandwich-like system composed of the p- or n-doped Si semiconductor, a polyelectrolyte cushion and a lipid bilayer.[3] Polyelectrolytes, including polyethylenimine, poly(styrene sulfonate) and poly(allylamine) were alternatively deposited onto negatively charged silica surface using a straightforward layer-by-layer technique. The lipid bilayer formation was completed via addition and subsequent fusion of lipid vesicles holding charge opposite to the underlying support. With the Optical Reflectometry (OR) and the Fluorescent Recovery After Photo-bleaching (FRAP) we could follow deposition of polyelectrolytes and lipid bilayer/intact lipid vesicles. The electrical properties of bare and modified Si semiconductors hold at different bias potentials were studied with the Electrochemical Impedance Spectroscopy (EIS). Optimized bio-interface will be further investigated for sensing applications.

References

1. M. Mescher, L. C. P. M de Smet, E. J .R. Sudhölter. J. H. Klootwijk *J. Nanosci. Nanotechnol.* **2013**, *13*, 5649.
2. L.C.P.M de Smet, D. Ullien, M. Mescher and E.J.R. Sudhölter, Organic Surface Modification of Silicon Nanowire-Based Sensor Device, Nanowires – Implementations and Applications, Abbass Hashim (Ed), InTech: Rijeka, **2011.**
3. L. Poltorak, M.L. Verheijden, D. Bosma, P. Jonkheijm, L. C. P. M. de Smet, E. J. R. Sudhölter, *submitted*, **2017**.

P31. Detection of Small Organic Compounds Based upon the Surface Plasmon Resonance of a Gold/ITO Structure

Camelia Popescu,[a,b] Andrei C. Popescu,[a] Rodica Cristescu,[a]
Michael Kompitsas,[c] Camelia Bala[b]

[a] *National Institute for Lasers, Plasma and Radiation Physics, Bucharest-Magurele, Romania*
[b] *University of Bucharest, Department of Analytical Chemistry,*
Faculty of Chemistry, Bucharest, Romania
[c] *National Hellenic Research Foundation, 11635 Athens, Greece*
camelia.popescu@inflpr.ro

Surface plasmon resonance (SPR) of metal nanoparticles is the fundamental principle behind many biosensor applications. In this work, by monitoring the reflected light from a prism coupler as a function of incident light angle or wavelength, a system for cholesterol detection has been developed.

Using an Nd:YAG laser source (l = 355 nm, τ = 10 nsec, v= 10 Hz), transparent conductive oxide (ITO) thin film waveguides were grown by Pulsed Laser Deposition (PLD) in low-pressure O_2 ambient. In a subsequent step, noble metal nanoparticles (Au) were sputtered on their surface by UV laser ablation. The influence of parameters upon sensing capability has been investigated in a thorough study by focusing on (a) thickness, (b) crystalline structure of the waveguides, (c) size and density of noble metal nanoparticles deposited on surface. This was achieved by a systematic change of a number of independent deposition parameters (pressure inside the deposition chamber, deposition substrate temperature, target-substrate separation distance, laser fluence and repetition frequency, number of applied laser pulses). All structures were studied in terms of transparency for λ = 633nm, the wavelength of the He-Ne laser source used for optical interrogation. We selected for coating with nanoparticles only the thin films with absorbance values lower than 15%.

Deposition of transparent conductive ITO films was mainly influenced by the substrate temperature and pressure inside the reaction chamber. The SPR signal correlated with AFM images allowed the identification of the optimal Au amount on the ITO films.

References

1. C.M. Miyazaki, Shimizu F.M., J.R. Mejía-Salazar, O.N. Oliveira, M. Ferreira *Nanotechnology* **2017**, *28*, 145501.
2. C. Rhodes, M. Cerruti, A. Efremenko, M. Losego, D. E. Aspnes, J.-P. Maria, S. Franzen, *J. Appl. Phys.*, **2008**, *103*, 093108.
3. C.C. Chang, N.F Chiu, D.S. Lin, Y. Chu-Su, Y.H. Liang, C.W. Lin *Anal. Chem.* **2010**, *82*, 1207.

P32. Interactions of Hydrophobic Magnetic Nanoparticles with Lipid Bilayers

Aleksandra Rękorajska, Sławomir Sęk, Paweł Krysiński

Department of Chemistry, University of Warsaw, Warsaw, Poland
ajoniec@chem.uw.edu.pl

Magnetic nanoparticles are widely used in many areas of life, for example in industry or medicine. Such a rapid usage requires investigations of nanoparticles impact on lipid structures.

Iron oxide nanoparticles (SPION) are gaining much of scientific attention due to their unique, superparamagnetic properties. This can be useful in targeted therapies – they can be guided in external magnetic field to desired tissues. It is crucial to investigate how the presence of hydrophobic SPIONs influences lipid bilayers properties. This is an important issue, because this kind of nanoparticles can be embedded in liposomes' bilayer, and be used as systems for targeted drug delivery and subsequent drug release.

We showed, that in the case of SPIONs present in the biomimetic membrane it becomes more stiff, and therefore is more likely to rupture when the system is treated with alternating magnetic field.[1] AFM-based mapping (supported membranes) and electrostriction studies (free-standing membranes) revealed, that bilayer lipid membranes formed from dioleylphosphatidylcholine and dipalmitoylphosphatidylcholine are less homogenous when they contain nanoparticles. These effects are slightly dependent on the amount of SPIONs – even small amount, such as 4% wt. increases the value of modulus of elasticity and decreases capacitance changes after voltage is applied.

Due to these effects the liposomes containing SPIONs in their bilayer and drug in their interior can release this drug when they are subjected to the external alternating magnetic field.

Acknowledgments

AR thanks Ministry of Science and Higher Education for financial support (Diamond Grant, project no. DI2013 017243).

References

1. A. Joniec, S. Sęk, P. Krysiński *Chem. – Eur. J.* **2016**, *22*, 17715.

P33. Electrodes Modified with Nitrogen and Sulfur Dual-doped Graphenes for Simultaneous Electrooxidation of Ascorbic Acid, Dopamine and Uric Acid

Natalia Rostkowska,[a] Hsuan-Fu Wang,[b] Marcin Holdynski,[a]
Magdalena Michalak,[a] Chi-Chang Hu,[b] Marcin Opallo[a]

[a]*Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[b]*Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan*
nrostkowska@ichf.edu.pl

Nowadays graphene (a single layer of graphite) attracts numerous research groups due to its high electrical conductivity, large specific surface area and electrocatalytic properties.[1] Doping graphene with heteroatoms changes its structure, band gaps and electrical properties.[2] Recent experiments show that dual-doped graphene (especially N with other element such as S, B, P) increases the electrochemical properties of this material, due to the synergetic effect between two heteroatoms, which comes from coupling interaction between them.[3]

In this work two samples of N, S dual doped graphenes have been prepared using microwave plasma torch with different content of nitrogen and sulfur. Scanning electron microscopy (SEM), Scanning Electrochemical Microscopy (SECM), X-ray and Raman spectroscopies were used to characterize this samples. Screen-printed carbon electrodes modified with N, S dual doped graphenes by droplet deposition were applied for simultaneous electrooxidation of ascorbic acid, dopamine and uric acid. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used for electrochemical determination of this compounds.

Ascorbic acid, dopamine and uric acid are essential biomolecules, e.g. in holding the regular physiological function of metabolism. Simultaneously determination of this compounds is very important in a fields of diagnostic, biochemistry and neurochemistry.[4]

References

1. A. K. Geim, K. S. Novoselov *Nat. Mater.* **2007**, *6*, 183.
2. T. O. Wehling, K. Novoselov, S. V. Morozov *et al. Nano Lett.* **2008**, *8,* 173.
3. J. Liang, Y. Jiao, M. Jaroniec, S.Z. Qiao *Angew. Chem. Int. Ed.* **2012**, *51*, 11496.
4. P. Kalimuthu, S. A. John *Bioelectrochemistry* **2009**, *7,* 13.

P34.

Synthesis and Electro-optical Properties of New Electrochromic Polymers-based on Dithienopyrrole Units

Renata Rybakiewicz,[a] Łukasz Skórka,[b] Małgorzata Zagórska,[b]

[a] *Faculty of Mathematics and Natural Sciences, School of Sciences,*
Cardinal Stefan Wyszynski University, Warsaw, Poland
[b] *Faculty of Chemistry, Warsaw University of Technology, Warsaw, Poland*
r.rybakiewicz@uksw.edu.pl

Dithienopyrrole-based (DPT) low and high molecular mass organic semiconductors are of growing scientific interest because of their potential use as active materials in electronic devices. DTP are attractive due to their high planarity, strong electrondonating ability of nitrogen atoms and a relatively long conjugation length of the fused-ring structure. In addition, these materials can be modified to tune their optical and electrical properties through control of a functional group, conjugation length, or the backbone structure. Several solution processable molecules[1] and macromolecules[2] containing dithienopyrrole derivatives have already been reported.

In this work we present the synthesis of new, solution processable, electroactive molecules, based on dithienopyrrole units (Fig 1). We also report a detailed spectroscopic, electrochemical and spectroelectrochemical characterization of these compounds and support the obtained experimental results by the DFT calculations.

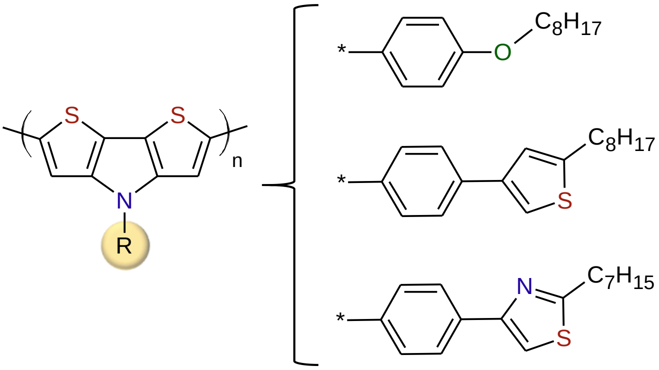


Fig. 1. Chemical formulas of the investigated DTP derivatives.

References

1. R. Rybakiewicz, Ł. Skórka, S. Pluczyk, P. Zassowski, D. H. Apaydin, E. D. Głowacki, M. Łapkowski, M. Zagórska, A. Proń *Chem. – Eur. J.* **2017**, *23*, 2839.
2. H.-G. Jeong, B. Lim, S.-I. Na, K.-J. Baeg, J. Kim, J.-M. Yun, D.-Y. Kim, *Macromol. Chem. Phys.* **2011**, *212*, 2308.

P35. Enhancing the Performances of Enzyme Biosensors for Plant Extracts by Using Nanoparticles and Polymers

Adrian Serban, Melinda David, Monica Florescu*

Faculty of Medicine, Transilvania University of Brasov, Brasov, Romania
*florescum@unitbv.ro

Enzyme biosensors offer a label-free screening method to determine bioactive compounds in plant extracts. Enzyme immobilization methods play an important role for biosensor performance, protecting enzyme bioactivity and it's successfully integration onto the electrode surface. The use of conducting polymers and nanomaterials is herewith of great importance.

In this work, we focused on biosensor performance improvement, using two enzyme entrapment methods on polymer modified gold electrode surface: 1) cross-linking and 2) Layer-by-Layer. Thus, a tyrosinase-based biosensor was developed for phenols detection. Gold electrodes were previously modified with cobalt (II)-porphyrin polymeric film, upon which tyrosinase was cross-linked. Layer-by-Layer method was used to modify gold electrodes surface for glucose detection. Glucose oxidase and a variety of carbon nanomaterials were dispersed in the positively-charged polymer chitosan, together with the negatively charged polymer poly(styrene sulfonate), PSS^-. The multilayer assembly was electrostatically adsorbed onto a conducting poly(3,4-ethylenedioxythiophene) (PEDOT) film.

Imaging methods were used for surface characterization, while electrochemistry (Figure 1) and surface plasmon resonance were used for biosensor evaluation. By optimizing sensing parameters, selective detection of phenols and glucose was facilitated in both situations with very good sensitivity and detection limit in nanomolar range. Biosensors were tested in both cases in the presence of plant extracts and obtaining good results.

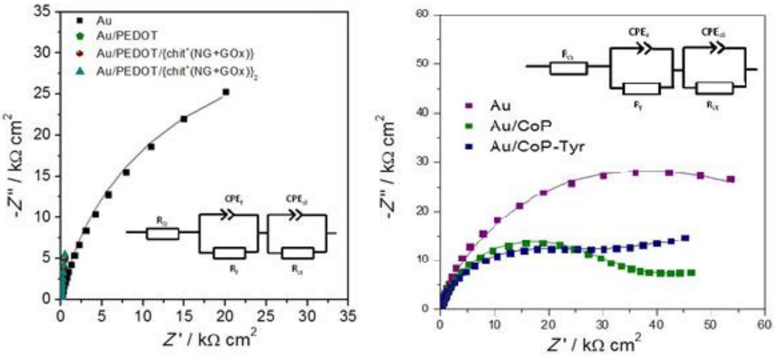


Figure 1. Complex plane plots for Au/PEDOT/{chit$^+$(NG+GOx)}$_2$ and Au/CoP-Tyr biosensors in 0.1 M NaPB, at −0.2 V vs. Ag/AgCl with the inset showing the equivalent electrical circuit used to fit the spectra.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-2801. We hereby acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, No 11/2009 for providing the infrastructure used in this work.

References

1. M. Florescu, M. David *Sensors* **2017**, *17*, 1314.
2. M. David, M. Florescu, M. M. Barsan, C. M. A. Brett *Procedia Technology* **2017**, *17*, 304.

P36. Silver Nanoparticles as a Risk Nanomaterial in the Production of ROS and DNA Damage

Jozef Sochr,[a] Anastasios Koutsogiannis,[b] Jana Blaškovičová,[a] Ján Labuda,[a]

[a] *Slovak University of Technology in Bratislava, Bratislava, Slovak Republic*
[b] *Aristotle University of Thessaloniki, Thessaloniki, Greece*
jozef.sochr@stuba.sk

Silver nanoparticles (AgNPs) are very attractive material due to their antibacterial, antimicrobial properties for the use in medicine, cosmetics, clothing industry. In addition, due to their electrical properties they are incorporated in electronics and used in electrochemistry for the preparation and development of biosensors[1,2].

At the same time, AgNPs represent a potential risk associated with their short-term and long-term toxicity because they can enter into almost all parts of the body. Some studies reported-a negative effect of AgNPs in term of DNA damage including an induction of oxidative stress – a formation of radicals. Excessive radical production leads to damage of cellular components including proteins, lipids, DNA and to cell necrosis[3].

The aims of this work were to detect generation of reactive oxygen species (ROS) at the UV-C irradiation (254 nm) of AgNPs of about 12 nm and 65 nm size in solution and to assess damage to DNA under these conditions using a DNA modified glassy carbon electrode. The generation of ROS was confirmed by the spectrophotometric agent 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl). The larger AgNPs have been found to be more active in the superoxide generation. ROS trapping in the presence of 100 μM calf thymus double stranded DNA (ct dsDNA) was also observed. AgNPs were applied in construction of the DNA-based biosensor prepared using layer-by-layer technique. Damage to DNA was evaluated using voltammetric measurements of the DNA responses after irradiation of the AgNPs and DNA layer by the UV light.

Acknowledgements

This work was supported by the Scientific Grant Agency VEGA of the Slovak Republic (Project 1/0489/16).

References

1. V. Banerjee, K.P. Das *Colloids Surf. B* **2013**, *111*, 71.
2. D. K. Ban, S. Paul *Colloids Surf. B* **2016**, *146*, 577.
3. A. S. Lavado, V. M. Chauhan, A. A. Zen, F. Giuntini, D. R. E. Jones, R. W. Boyle, A. Beeby, W. C. Chan, J. W. Aylott *Nanoscale* **2015**, *7*, 14525.
4. R. O. Olojo, R. H. Xia., J. J. Abramson *Anal. Biochem.* **2005**, *339*, 338.

P37. Geometrically Constrained Plasmonic Nanostructures for Sensing

Karolina Sulowska,[a] Ewa Roźniecka,[b] Justyna Grzelak,[a,c] Michał Ćwik,[b]
Joanna Niedziółka-Jönsson,[b] Sebastian Maćkowski,[a,c]

[a] *Institute of Physics, Faculty of Physics, Astronomy and Informatics,*
Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[b] *Institute of Physical Chemistry Polish Academy of Sciences,*
Kasprzaka 44/52, 01-224 Warsaw, Poland
[c] *Baltic Institute of Technology, Al. Zwycięstwa 96/98, Gdynia, Poland*
mackowski@fizyka.umk.pl

Among several critical challenges faced by nanotechnology is development of advanced structures with defined geometry and predictable function. It involves not only reproducibility of homogenous nanostructure fabrication and synthesis, but also establishing standard, reliable methods of nanostructure manipulation. In the context of this work, we intend to exploit the unique properties of metallic nanostructures associated with plasmonic excitations and underline the importance of spatial organization thereof for straightforward optical detection.

The first type of plasmonic nanostructure is silver island film (SIF) deposited in a controlled way on a substrate. As the enhancements of the optical response can be as high as hundred-fold, simple imaging should allow for immediate determination of surface-analyte interaction. On the other hand, geometrical constrain can be provided itself by the type of metallic nanostructures. In particular, metallic nanowires with defined elongated shape, offer such a functionality. This, in connection with efficient functionalization schemes, can be successfully applied for detecting multiple analytes, either optically or electrically.

Acknowledgements
Research was partially financed by the National Science Centre (Poland) within the OPUS grant no 2016/21/B/ST3/02276 and the project 3/DOT/2016 funded by the City of Gdynia, Poland.

P38. Electrode Surface Modification by Electrochemical Co-deposition of Redox Polymers and Biocatalysts

Julian Szczesny,[a] Adrian Ruff,[a] Sónia Zacarias,[b] Inês A. Pereira,[b]
Nicolas Plumeré,[c] Wolfgang Schuhmann,[a]

[a] *Analytical Chemistry – Center for Electrochemical Sciences (CES),*
Ruhr-Universität Bochum, D-44870 Bochum, Germany
[b] *Instituto de Tecnologia Quimica e Biologica Antonio Xavier,*
Universidade Nova de Lisboa, 2780-157 Oeiras, Portugal
[c] *Center for Electrochemical Sciences (CES) – Molecular Nanostructures,*
Ruhr-Universität Bochum, D-44870 Bochum, Germany

A major challenge in the development of bioelectrochemical devices is the immobilization and electrical connection of biocatalysts to an electrode surface. Redox polymers are widely used for the electrical wiring and immobilization of various biocataylsts.[1]

Typically, the electrodes are modified by a manual drop-cast process. This method is unfavorable for large scale production, modification of micro- and nanoelectrodes or for the modification of complex electrode geometries. Moreover, the drop-cast process often leads to rather thick films, where the current response is limited by electron transfer or substrate diffusion within the film. Furthermore, the formation of very thin films, which ensure a fast current response due to a fast diffusion of substrate is challenging, but crucial for the fabrication of efficient and sensitive biosensors. A non-manual deposition based on electrochemical methods may overcome these limitations. Here, the deposition process can be controlled by selecting appropriate potentials or the pulse width during the deposition, which usually allows for the control over the film thickness and catalyst loading. Combined with an electrochemically induced crosslinking process, long term stable polymer/enzyme films can be formed, as it was demonstrated for the amperometric detection of glucose by glucose oxidase entrapped in a crosslinked, electrodeposited paint.[2] Hydrogenases are nature's efficient catalyst for the reversible conversion of H_2 to protons. These enzymes reveal high activities towards the oxidation of H_2 and thus they are also used as biocatalyst in highly sensitive hydrogen sensors.[3] However, in this case a drop cast process was used for film formation. Here, we present the development of a bioanode comprising a highly active [NiFeSe] hydrogenase from *Desulfovibrio vulgaris* Hildenborough (*Dv*H) by an electrochemically induced co-deposition of the biocatalyst and a specifically designed viologen-modified redox polymer. The co-deposition is based on the electrochemical *in-situ* activation of a protected bifunctional crosslinker, which reacts with anchoring sites in the viologen modified polymer. By this, a dense and crosslinked polymer network that entraps the biocatalyst on the electrode surface is formed.[4] The deposition is induced by applying short anodic potential pulses. The amount of deposited polymer and hence the film thickness can be controlled by varying the number of repetitions of the potential pulse sequence. Thus, very thin polymer/enzyme films can be obtained, for which the catalytic response depends on the amount of the deposited biocatalyst. Moreover, the co-deposition with the enzyme yields highly active films, that are not limited by mass transport. In addition, the use of the *Dv*H [NiFeSe] hydrogenase in combination with the low potential, viologen modified polymer matrix allows for the complete reactivation of the hydrogenase after deactivation by O_2.

References

1. A. Ruff *Curr. Opin. Electrochem.* **2017**, DOI: 10.1016/j.coelec.2017.06.007 (*in press*).
2. S. Pöller, D. Koster, W. Schuhmann *Electrochem. Commun.* **2013**, *34*, 327.
3. F. Zhao, F. Conzuelo, V. Hartmann, H. Li, S. Stapf, M. M. Nowaczyk, M. Rögner, N. Plumeré, W. Lubitz, W. Schuhmann *Biosens. Bieoelectron.* **2017**, *94*, 433.
4. A. Ruff, J. Szczesny, S. Zacarias, I. A. C. Pereira, N. Plumeré, W. Schuhmann *ACS Energy Lett.* **2017**, *2*, 964.

P39. Fabrication of Carbon Nanoelectrodes by Pyrolysis of Petroleum Gas Inside Quartz Nanopipettes

Aleksandra Szymańska, Magdalena Michalak, Małgorzata Kurel,
Marcin Opałło, Wojciech Nogala

Institute of Physical Chemistry, Polish Academy of Sciences,
ul. Kasprzaka 44/52, PL-01224 Warsaw, Poland
aszymanska@ichf.edu.pl

Nanometer-sized electrodes are utilized to research in many laboratories worldwide.[1] They were used to study electrochemical and biological systems on the nanoscale including electrochemistry of single entities, such as redox molecules,[2] enzyme molecules,[3] nanobubbles,[4] nanoparticle sizing by impact coulometry,[5] as well as processes inside biological cells.[6]

Besides many electronically conductive materials composing nanoelectrodes, pyrolytic carbon is one of the most desirable due to wide potential window of such electrodes and possibility of modification. Carbon nanoelectrodes obtained by chemical vapor deposition inside a quartz nanopipettes were employed in various researches in a few laboratories. They were used as scanning electrochemical microscopy (SECM) tips for nanoscale chemical imaging,[7,8] intracellular analysis,[9] or SECM pH mapping.[10]

In this poster fabrication procedure of carbon nanoelectrodes by pyrolysis of petroleum gas inside quartz nanopipettes will be presented in details. Next step of this study is to employ carbon nanoelectrodes for determination of silver species inside bacteria.

References

1. Y. Ying, Z. Ding, D. Zhan, Y. Long *Chem. Sci.* **2017**, *8*, 3338.
2. P. Sun, M. V. Mirkin *J. Am. Chem. Soc.* **2008**, *130*, 8241.
3. L. Han, W. Wang, J. Nsabimana, J. Yan, B. Ren, D. Zhan *Faraday Discuss.* **2016**, *193*, 133.
4. H. Ren, S. German, M. Edwards, Q. Chen, H. White *J. Phys. Chem. Lett.* **2017**, *8*, 2450.
5. J. Clausmeyer, P. Wilde, T. Löffler, E. Ventosa, K. Tschulik, W. Schuhmann *Electrochem. Commun.* **2016**, *73*, 67.
6. Y. Wang, J-M. Noel, J. Velmurugan, W. Nogala, M. V. Mirkin, C. Lu, M. G. Collignon, F. Lemaitre, C. Amatore *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109*, 11534.
7. Y. Takahashi, A. Shevchuk, P. Novak, Y. Zhang, N. Ebejer, J. Macpherson, P. Unwin, A. Pollard, D. Roy, C. Clifford, H. Shiku, T. Matsue, D. Klenerman, Y. Korchev *Angew. Chem. Int. Ed.* **2011**, *50*, 9638.
8. K. McKelvey, B. Nadappuram, P. Actis, Y. Takahashi, Y. Korchev, T. Matsue, C. Robinson, P. Unwin *Anal. Chem.* **2013**, *85*, 7519.
9. P. Actis, S. Tokar, J. Clausmeyer, B. Babakinejad, S. Mikhaleva, R. Cornut, Y. Takahashi, A. Lopez Cordoba, P. Novak, A. Shevchuck, J. Dougan, S. Kazarian, P. Gorelkin, A. Erofeev, I. Yaminsky, P. Unwin, W. Schuhmann, D. Klenerman, D. Rusakov, E. Sviderskaya, Y. Korchev *ACS Nano* **2014**, *8*, 875.
10. M. Michalak, M. Kurel, J. Jedraszko, D. Toczydlowska, G. Wittstock, M. Opallo, W. Nogala *Anal. Chem.* **2015**, *87*, 11641.

P40. A Novel Electrochemical Sensor Based on Modified Ni Electrodes for Formaldehyde Detection in Alkaline Media

S. Trafela,[a,b] X. Xu,[a,b] S. Kobe,[a,b] K. Žužek-Rožman[a,b]

[a] *Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia*
[b] *Jožef Stefan International Postgraduate School, Ljubljana, Slovenia*
spela.trafela@ijs.si

In this study we used KOH-modified Ni electrodes (films and nanowires) for the electro-oxidation of formaldehyde (HCHO), which are promising to be used as effective electrochemical receptor element. Ni ''films'' were deposited on Au substrates by the electro-deposition from acidic and neutral $NiSO_4$-based solutions with subsequent modification in 0.1 M KOH. From the SEM results we found out that pH of Ni^{2+} solution affects the morphology of the deposited films. Under acidic conditions homogeneous Ni film was formed, but under neutral conditions porous Ni film was deposited. Ni nanowires (200 nm diameter) were prepared with template-assisted electrodeposition into alumina templates. After the electro-deposition of the nanowires, the template was removed in 10 M solution of NaOH in order to get free standing wires.

The modification step with KOH is very important for the further investigations of HCHO oxidation, because $NiO(OH)/Ni(OH)_2$ redox couple exhibits high catalytic activity towards HCHO. The electro-catalytic activity of modified Ni nanowires and Ni films (Ni-OOH) for formaldehyde detection in alkaline media was investigated via a series of electrochemical measurements. The potential range for modification in KOH has to be chosen in the region where oxygen does not form (the maximum potential 0.6V), because molecular oxygen can be adsorbed on the electrode and inhibits further oxidation of HCHO.[1]

Experimental results show that the 2D and 1D Ni-based electrode (nanowires and films) displays a remarked electro-catalytic activity for the oxidation of HCHO and exhibit a linear relationship in a concentration range from 1 mM to 0.5 M. An oxidation peak was obtained at potentials around 0.5 V vs. Ag/AgCl for concentrations 1 mM – 100 mM and around 0.8 V vs. Ag/AgCl for concentrations above 0.1 M. Results showed that the reaction of the electro-oxidation most probably proceeds by a chemical reaction with NiO(OH) as shown on Scheme 1. The experimental data further reveal that Ni nanowires exhibits a higher sensitivity (approximately 7x higher) compared to the homogeneous and porous Ni electrode, because the slope of the curve current signals vs. concentrations reached higher value. The detection limit was 0.2 mM/cm^2 for Ni nanowires, 0.5 mM/cm^2 for porous Ni film and 0.8 mM/cm^2 for homogeneous Ni film. The current values were normalized on the surface areas, determined by an oxalate method for measuring the electrochemically active Ni surface areas. It was concluded from results that Ni nanowires exhibit a higher catalytic activity due to the larger surface to volume ratio and connected higher amounts of adsorbed –OOH groups on the surface that promote the electron transfer between receptor elements and HCHO molecules.

$$\text{NiO(OH)} + \text{formaldehyde} \longrightarrow \text{oxidized formaldehyde} + \text{Ni(OH)}_2$$

Scheme 1. Formaldehyde oxidation on modified Ni electrodes

References

1. S. Maximovitch, G. Bronoel *Electrochimica Acta* **1981**, *26*, 9, 1331.

P41. Optical Chemosensor for Protein Determination with Molecularly Imprinted Polymer Recognition and Birefringence Liquid Crystal Detection

Maciej Cieplak,[a] Rafał Węgłowski,[b] Zofia Iskierko,[a] Dorota Węgłowska,[b] Piyush S. Sharma,[a]
Krzysztof Noworyta,[a] Francis D'Souza,[c] and Wlodzimierz Kutner[a,d]

[a] *Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[b] *Faculty of Advanced Technologies and Chemistry,*
Military University of Technology, Warsaw, Poland
[c] *Department of Chemistry, University of North Texas, Texas, United States*
[d] *Faculty of Mathematics and Natural Sciences, School of Sciences,*
Cardinal Stefan Wyszynski University, Warsaw, Poland
dorota.weglowska@wat.edu.pl

Since Abbott's group reported on the use of a 4-pentyl-4′-cyanobiphenyl (5CB) liquid crystal (LC) as the sensing element of a chemosensor for optical determination of IgG[1],[2] and avidin (Av)[1] interaction with biotin, it has become apparent that biomolecules deposited on a solid surface may affect reorientation of the liquid crystal (LC) molecules.[3] Reorientation of these molecules generates optical response seen under a polarized-light optical microscope. This phenomenon was used for devising biosensors for determination of proteins.[4]

In the present work, we have developed a novel optical liquid crystalline chemosensor with a recognition film of molecularly imprinted polymer (MIP), templated with human serum albumin (HSA) molecules, deposited by electropolymerization. The HSA analyte binding affects LC molecules orientation causing a change in light intensity passing through the sensing unit, thus allowing for detection and quantification of the analyte. To gain precise control over the HSA imprinting, we used a semi-covalent imprinting strategy introduced in our previous study.[5] The procedure developed herein allowed determining HSA in the concentration range of 3.03 to 15.15 nM with the limit of detection of 250 μg/mL and the appreciable apparent imprinting factor of 3.3.

References

1. V. K. Gupta, J. J. Skaife, T. B. Dubrovsky, N. L. Abbott, *Science,* **1998**, *279*, 2077.
2. S. R Kim, N. L. Abbott *Adv. Mater.* **2001**, *13*, 1445.
3. C. Y. Xue, K. L. Yang *Langmuir* **2008**, *24*, 563.
4. B. H. Clare, N. L. Abbott *Langmuir* **2005**, *21*, 6451.
5. M. Cieplak, K. Szwabinska, M.; Sosnowska, K. C. C. Bikram, P. Borowicz, K. Noworyta, F. D'Souza, W. Kutner *Biosens. Bioelectron.* **2015**, *74*, 960.

P42.

Development of a Cefdinir Selective Optical Sensor Based on Inorganic Molecularly Imprinted Polymers Coated Mn-doped ZnS Quantum Dots

H. Yılmaz, N. Ertaş, H. Basan

Gazi University, Faculty of Pharmacy, Department of Analytical Chemistry,
06330, Ankara, Turkey

A new room temperature phosphorescent (RTP) sensor based on quantum dots (QDs) and surface molecularly imprinted inorganic polymer (IMIP) was developed for the recognition of cefdinir (CEF). The Mn-doped ZnS QDs were prepared using procedure described by Wang *et al.* with slight modification.[1] Then, QDs were decorated with 3-(mercaptopropyl)triethoxy silane (MPTS) to increase the stability of the particles. The IMIP was mainly synthesized using CEF, 3-aminopropyltrimethoxy silane (APTES), and tetraethoxy silane (TEOS) as the template, functional monomer, and cross-linker, respectively. Non-imprinted inorganic polymer (INIP) was also obtained using the same procedure but in the absence of template. Degree of correlation between quenching of phosphorescence signal and CEF concentration was studied during the binding studies. This study was performed using different binding organic and aqueous (pH 4-8) media and calibration curve for the developed sensor was constructed by applying the Stern-Volmer equation.

References

1. H. F. Wang, T. R. Ji, X. P. Jan *Anal. Chem.* **2009**, *81*, 1615.

P43. Monitoring of Na^+/K^+-ATPase Activity in Lipidic Cubic Phase by Electrochemical and Spectroscopic Methods

Martina Zatloukalova,[a,b] Ewa Nazaruk,[a] David Novak,[b]
Jan Vacek,[b] Renata Bilewicz[a]

[a] *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland*
[b] *Department of Medical Chemistry and Biochemistry, Faculty of Medicine and Dentistry, Palacky University, Hnevotinska 3, Olomouc 775 15, Czech Republic*
martina.zatloukalova@seznam.cz

Lipidic cubic phases (LCPs) are well recognized as suitable membrane-mimetic matrices for the stabilization and crystallization of membrane proteins. However, the activity of most of these proteins in the LCP environment was not investigated. The goal of our work was the incorporation of Na^+/K^+-ATPase transmembrane protein into monoolein-based LCP with subsequent verification of the protein activity.

Pn3m symmetry of LCP without and with incorporated Na^+/K^+-ATPase was identified by small-angle X-ray scattering measurement. No significant differences were found in structure parameters of LCP without and with incorporated Na^+/K^+-ATPase. We assume that Na^+/K^+-ATPase is incorporated inside the cubic phase aqueous channels and does not affect the shape of lipid phases.

The activity of Na^+/K^+-ATPase in LCP was studied spectroscopically[1] and using different electrochemical methods, where an LCP-modified glassy carbon electrode was used. The enzyme activity evaluation is based on the ability of Na^+/K^+-ATPase to hydrolyze ATP to form ADP and free phosphate, reacting with ammonium molybdate and formed phosphomolybdate complex under acidic condition. Blue colored phosphomolybdate complex was determined in presence of ascorbic acid by spectroscopy at 710 nm and voltammetry. The voltammetric peak at ca. +0.2 V *vs.* Ag/AgCl/3M KCl was used to monitor phosphate released in the presence or absence of specific protein inhibitor, ouabain. In addition to ATP-hydrolyzing activity, the amperometric measurement of the current passing through the LCP film was carried out. K+- induced electrogenic transport produced by Na^+/K^+-ATPase incorporated in LCP was studied in the presence and absence of two inhibitors, ouabain and orthovanadate.

Acknowledgements

The authors wish to thank the Swiss National Science Foundation (Sinergia project no. CRSII2 154451) and Palacky University for institutional support (RVO: 61989592).

References

1. M. Kubala, J. Geleticova, M. Huliciak, M. Zatloukalova, J. Vacek, M. Sebela *Biomed. Pap.* **2014**, *158,* 194.

Index

Last name	**First name(s)**	**Abstract**	**Page**
Palchetti	Ilaria	K21	118
Plumere	Nicolas	K12	78
Pollap	Aleksandra	P29	206
Poltorak	Lukasz	P30	208
Popescu	Camelia	P31	210
Radecka	Hanna	K02	24
Rękorajska	Aleksandra	P32	212
Rostkowska	Natalia	P33	214
Rybakiewicz	Renata	P34	216
Scherbahn	Vitali	SC11	84
Serban	Adrian	P35	218
Sęk	Sławomir	K16	90
Shani	Gidi	K15	88
Sharma	Piyush Sindhu	K11	70
Shleev	Sergey	T08	96
Sochr	Jozef	P36	220
Sulowska	Karolina	P37	222
Szczesny	Julian	P38	224
Szymańska	Aleksandra	P39	226
Trafela	Špela	P40	228
Trashin	Stanislav	SC03	42
Walcarius	Alain	K03	30
Węgłowska	Dorota	P41	230
Winkler	Krzysztof	T09	104
Wojciechowski	Kamil	K01	22
Yilmaz	Hüma	P42	232
Zatloukalova	Martina	P43	234
Zhao	Fangyuan	SC02	34
Zhurauski	Pavel	SC01	32

See you all
at the 9th International Workshop
of Chemical and Biochemical Sensing,
SMCBS'2019,
in November 2019

This book was set and edited
by Ievgen Obraztsov,
Institute of Physical Chemistry,
Polish Academy of Sciences
Warsaw, Poland, 2017
ISBN 978-83-939295-1-1