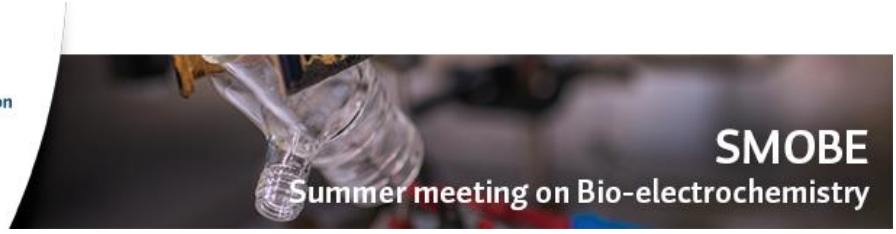
AXES
Antwerp X-ray Analysis, Electrochemistry & Speciation
University of Antwerp



Room K2.01

Kleine kauwenberg 14-22

B-2000 Antwerpen

ABSTRACTS

TUTORIAL LECTURES

LARS JEUKEN

L.J.C.Jeuken@leeds.ac.uk

Jeuken Group, University of Leeds

SUPRAMOLECULAR ELECTRODE ASSEMBLIES IN BIOELECTROCHEMISTRY

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

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 design of ever more complex systems. In this tutorial lecture, I will highlights developments over the last decade in supramolecular approaches. 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) Co-assembly of nanoparticles to enhance electroactive surface areas of electrodes; and (3) the use of layer-by-layer assembly.

(2) Many redox enzymes are oxidoreductases and an important group of them reside in bacterial, mitochondrial or chloroplast (inner) membranes. A brief overview will be given of strategies used to make electrodes suitable for membrane proteins.

(2) The electrochemical surface area of electrodes can be greatly enhanced if either the electrode is structured or modified at length scales comparable to that of the redox proteins. Several key examples will be covered in this tutorial lecture, including mesostructured electrodes and electrodes modified with nanoparticles.

(3) Layer-by-Layer (LbL) deposition is used increase enzyme loading or to create well organized layers consisting of different enzymes in multistep catalysis. LbL systems either have to be permeable to electron mediators, which can be proteins, or the LbL system has to be conductive.

THOMAS DONEUX

tdoneux@ulb.ac.be

Chimie Analytique et Chimie des Interfaces, Université libre de Bruxelles (ULB)

ELECTROCHEMISTRY AND NUCLEIC ACIDS: A BRIEF TUTORIAL

In spite of its well-known advantages (miniaturisation and portability, sensitivity, rapidity), electrochemical DNA-based sensing is still far from a mainstream analytical tool in biosensing. Numerous reports in the literature, whether with apparently simple "model systems" (e.g. DNA hybridisation) or with more complex systems (e.g. aptamer-protein binding), are highly contradictory with respect to the claimed performance or even with respect to the signal variation (signal ON vs. signal OFF). In the opinion of the author, this is intrinsically a reproducibility issue which can be traced down to the interfacial architecture of the DNA biosensor, i.e. the modified electrode.

In this tutorial, simple directions are provided to overcome these problems along the following motto: "Know your DNA, know your electrochemistry".

Nucleic acids are polyelectrolytes (charged polymers) and are thus sensitive to the charge and electric field distributions -key quantities for electrochemists-. Importantly, nucleic acids are diverse in terms of secondary structure (Watson-Crick double-helix, aka "B-DNA", but also hairpins, i-motifs, G-quadruplex, Z-DNA...) and these structures are highly dynamic on the typical timescale of electrochemical experiments. They display a broad range of interactions (covalent, intercalation, groove binding...) with synthetic or natural ligands, many of them being electroactive. Redox "labels" and redox "markers" can be thus employed to transduce electrochemically the relevant biochemical information (hybridisation, target recognition).

Fortunately, the electrochemistry toolbox is well furnished. The experimentalist can choose among numerous redox species with different properties (formal potential, charge, reversibility) and states (dissolved or attached, covalently vs non-covalently), among various electrode materials (determining the potential windows and surface chemistries), and among many electrochemical techniques (linear sweep, differential pulse or square wave voltammetries, ac voltammetry, impedance spectroscopies...). An ideal match between these candidates and the envisioned biosensor performance can usually be achieved through an appropriate experimental design.

This communication will focus on some selected work from the author's laboratory to illustrate these concepts and show how the getting the basics right in electrochemistry and in nucleic acids can help devising proper electrochemical DNA biosensors.

ELISABETH LOJOU

lojou@imm.cnrs.fr

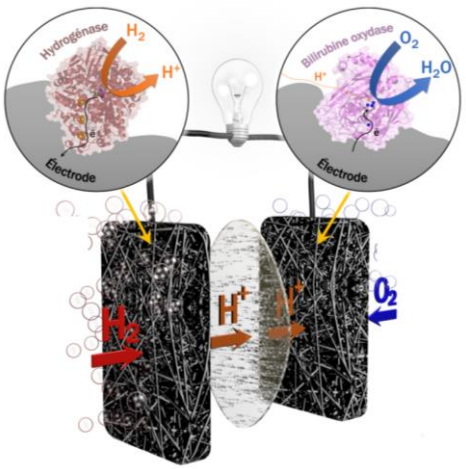
BIP, CNRS-Aix Marseille University

ENZYME ELECTRICAL CONNECTION FOR ENZYMATIC FUEL CELLS

Biology offers an attractive alternative to noble metal catalysts thanks to the use of biodegradable, efficient and specific enzymes as biocatalysts in enzymatic fuel cells. Simply considering the size of the biological object with the active site buried inside the isolating protein moiety, strategies must be, however, engaged to succeed first in the electrical connection of the enzymes.

We will examine the molecular factors that affect the interfacial electron transfer rate between a protein and an electrode surface. By taken examples from the recent literature, we will show how microorganisms are organized so as this electron transfer is not the limiting step. We will then extend our approach to the case of the interaction between enzymes and electrode surfaces, and show that one key issue is the orientation of the biological object [1]. We will present some chemical modifications of the electrodes that can control the biocatalyst orientation, then the electron transfer rate, and finally the catalysis.

Then, we will demonstrate that an efficient orientation of an enzyme on an electrode is not sufficient for most applications. We will then emphasize the researches made toward the development of 3D networks for efficient incorporation of high amount of enzymes [2]. This includes metal or carbon nanoparticles, but also other carbon nanomaterials (Nanotubes, nanofibers, felt…). We will conclude by presenting the very recent projects devoted to the development and applications of a new generation of biofuel cells [3, 4].



[1] A. Ciaccafava et al., Angew. Chem. Int. Ed., (2012) ; A. Ciaccafava et al., Electrochem. Com., (2012) ; F. Oteri et al., PCCP (2014) ; C. Gutierrez-Sanchez et al., ACS Catalysis (2016)

[2] A. De Poulpiquet et al., PCCP, (2014) ;. K. Monsalve et al., Bioelectrochem. (2015) ; I. Mazurenko et al. ACS AMI (2016)

[3] A. de Poulpiquet et al., Electrochem. Com., (2014); K. Monsalve et al., Electrochem. Commun. (2015); I Mazurenko et al. EES (2017)

[4] I. Mazurenko et al., Sust. Energ. & Fuels (2017)

KEYNOTE LECTURES

ILARIA PALCHETTI

ilaria.palchetti@unifi.it

Dipartimento di Chimica, Università degli Studi di Firenze

NOVEL ELECTRODE MATERIALS AND ARCHITECTURES FOR ENZYME AMPLIFIED NUCLEIC ACID BIOSENSING

In the development of nucleic acid hybridization biosensors, the electrochemical measurement of a catalytic product from a captured enzyme label such as horseradish peroxidase (HRP) or alkaline phosphatase (AP) can be used as a measure of hybridization. Enzymatic amplification of the binding event allows very sensitive measurements of the target DNA or RNA. However, the catalytic activity, the electron transfer and chemical reactivity of the electrode material as well as the electrode surface area itself, can affect the biosensor sensitivity and selectivity. Thus, the choice of the electrode material and architecture should be carefully evaluated, in order to find the optimal biosensing strategy. The behaviour of a carbon electrode modified by layers of reduced graphene oxide flakes, uniformly coated by a dense layer of Au nanoparticles, is, herein, discussed. Furthermore, the modification of nanostructured TiO_2 electrodes by the product of the enzymatic reaction labelling the hybridization events, is also illustrated. This photosensitization process allows the photoelectrochemical detection of a miRNA target sequence, under visible-light illumination.

LO GORTON

Lo.Gorton@gmail.com

Institute of Chemistry, Lund University

ELECTROCHEMICAL COMMUNICATION BETWEEN BACTERIAL CELLS AND ELECTRODES

Electrochemical transfer communication between bacterial cells/biological membranes and electrodes can be obtained through the use of freely diffusing monomeric redox mediators. We have, however, also shown that flexible osmium redox polymers can work as efficient mediators for a number of both Gram– as well as Gram+ bacteria [1, 2]. This presentation will cover two aspects of our current research in this area: (1) Electrochemical communication between whole viable photosynthetic bacterial cells as well as with eukaryote systems (thylakoid membranes from spinach, eukaryote algae) and electrodes through the use of Os polymers [3-5]. 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 [6, 7]. (2) To be able to understand how a redox-polymer can communicate with a bacterial cell we have also studied the role of each component of the comparatively simple respiratory chain of the Gram+ *Enterococcus faecalis* [8]. This bacterium is a facultative anaerobe and aerobic respiration depends on the presence of heme, which serves as a cofactor for cytoplasmic catalase and membrane bound cytochrome *bd* oxidase. *E. faecalis* does not require heme to grow and lacks the genes for its synthesis but is able to take up heme or its analogues from the environment. When the cells are supplied with heme, a minimal respiratory chain is built up, including several NADH dehydrogenases, a demethylmenaquinol pool in the membrane and the heme-dependent cytochrome *bd* oxidase. The wild type as well as three mutant strains of *E. faecalis* with mutations within the electron transport chain were investigated under different experimental and culture conditions to identify possible ways of the cell-electrode communication.

[1] K. Hasan, S. A. Patil, D. Leech, L. Gorton, *Biochem. Soc. Trans., 40 (2012) 1330-1335.*

[2] G. Pankratova and L. Gorton, *Curr. Opin. Electrochem., 5 (2017) 193–202.*

[3] K. Hasan, H. B. Yildiz, E. Sperling, P. Ó Conghaile, M. A. Packer, D. Leech, C. Hägerhäll, L. Gorton, *Physical Chemistry Chemical Physics, 16 (2014) 24676-24680*.

[4] H. Hamidi, K. Hasan, S. C. Emek, Y. Dilgin, H.-E. Åkerlund, P.-Å. Albertsson, D. Leech, L. Gorton, *ChemSusChem, 8 (2015) 990-993*.

[5] K. Hasan, E. Çevik, E. Sperling, M. A. Packer, D. Leech, L. Gorton, *Adv. Energ. Mater., 5(22) (2015).*

[6] G. Pankratova, D. Pankratov, K Hasan, H.-E. Åkerlund, P.-Å. Albertsson, D. Leech, S. Shleev, L. Gorton, *Adv. Energy Mater., 2017, 1602285.*

[7] G. Pankratova, D. Pankratov, C. Di Bari, A. Goñi-Urtiaga, M. D. Toscano, Q. Chi, M. Pita, L. Gorton, A. L. De Lacey, *ACS Appl. Energy Mater., 1(2) (2018) 319–323*.

[8] G. Pankratova, D. Leech, L. Gorton, L. Hederstedt, *Biochemistry, accepted,* **DOI:** 10.1021/acs.biochem.8b00600.

ALEXANDER KUHN

kuhn@enscbp.fr

Institute of Molecular Science, University Bordeaux

BIOMIMETIC METAL ELECTRODES FOR ENANTIOSELECTIVE ANALYSIS, SEPARATION AND SYNTHESIS

The development of materials with chiral features is a major scientific challenge due to a large number of potential applications ranging from sensing to catalysis and separation. In this contribution we report the elaboration of biomimetic electrodes with imprinted molecular recognition sites. We have synthesized chiral mesoporous metal by the electrochemical reduction of platinum salt in the simultaneous presence of a liquid crystal phase and chiral template molecules [1, 2]. The metal perfectly retains the chiral information after removal of the template and shows a significant discrimination between two enantiomers when using it as electrode in Differential Pulse Voltammetry. Such nanostructured metals are also able to break the symmetry during electrochemical synthesis [3]. We found that the R/S ratio of the synthesis product is not unity when using imprinted electrodes and can reach values over 90% [4]. In order to illustrate the general validity of this approach, we were able to extend the concept to several chiral template molecules, leading to chiral encoded nanostructures. Recently we could use such matrices also as stationary phases in microfluidic devices for the efficient separation of chiral molecules [5]. Therefore these biomimetic designed surfaces open new horizons for electroanalysis, separation science and enantioselective electrosynthesis.

[1] 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.

[2] T. Yutthalekha, C. Warakulwit, J. Limtrakul, A. Kuhn, Electroanalysis, 2015, 27: 2209.

[3] T. Yutthalekha, C. Wattanakit, V. Lapeyre, S. Nokbin, C. Warakulwit, J. Limtrakul, A.Kuhn, Nat. Comm. 2016, 7:12678.

[4] C. Wattanakit, T. Yutthalekha, S. Assavapanumat, V. Lapeyre, A. Kuhn, Nat. Comm. 2017, 8:2087

[5] S. Assavapanumat, A. Perro, N. Sojic, P. Garrigue, B. Goudeau, T. Yutthalekha, C. Wattanakit, A. Kuhn, 2018, submitted

PHILIP BARTLETT

pnb@soton.ac.uk

Department of Chemistry, University of Southampton

DIRECT ELECTRON TRANSFER AND MEDIATED ELECTRON TRANSFER – A TALE OF TWO ENZYMES

P. N. Bartlett, F. Al-Lolage and M. Meneghello

Glucose oxidase (EC 1.1.3.4) and cellobiose dehydrogenase (EC 1.1.99.18) are both flavin containing enzymes and both can be used to catalyse the electrochemical oxidation of glucose to gluconolactone. In the case of glucose oxidase, a homodimer, the two flavin redox centres and buried deep within the protein and direct electron transfer (DET) to electrode surfaces is not expected on grounds of the large distance between the active site and the surface of the native protein [1]. Despite this there are many papers in the literature that claim DET for glucose oxidase at nanostructured electrodes. Cellobiose dehydrogenase, has a flavin domain with a separate haem domain linked by a flexible peptide chain such that internal electron transfer can occur between the two.

In this lecture we will present results for the study of the two enzymes. In the case of glucose oxidase we will show that there is no evidence for DET for the native enzyme; the many published claims of DET are based on the misinterpretation of the data [2]. For cellobiose dehydrogenase we will present data for the immobilization of the enzymes in different orientations at the electrode surface [3]. The immobilized enzyme is found to be very stable and this allows us to study in detail, and to compare, the kinetics for DET and mediated electron transfer (MET) for the enzyme in different orientations.

1. G. S. Wilson, “Native glucose oxidase does not undergo direct electron transfer”, Biosens. Bioelectron., 82 (2016), pp. vi-vii.

2. P. N. Bartlett and F. Al-Lolage, “There is no evidence to support literature claims of direct electron transfer (DET) for native glucose oxidase (GOx) at carbon nanotubes or grapheme”, J. Electroanal. Chem., in press DOI: 10.1016/j.jelechem.2017.06.021

3. F. A. Al-Lolage, M. Meneghello, S. Ma, R. Ludwig and P. N. Bartlett, “A flexible method for the stable, covalent immobilization of enzymes at electrode surfaces”, ChemElectroChem, 4 (2017)1528-1534.

PATRICK WAGNER

PatrickHermann.Wagner@kuleuven.be

Soft-Matter Physics and Biophysics Section ZMB, Department of Physics and Astronomy, KU Leuven

THERMAL DETECTION OF CELLS AND BACTERIA WITH SYNTHETIC WHOLE-CELL RECEPTORS

In this contribution, I will give an overview on the biosensing principle of the heat-transfer method HTM and illustrate how the thermal-boundary resistance Rth of solid-liquid interfaces can be utilized in bio-analytical applications. HTM is conceptually related to impedance spectroscopy with the difference that electrical currents are replaced by thermal currents. Hence, HTM can be employed in situations with electrically insulating chip materials, receptor coatings and liquids. Then, I will illustrate this sensing principle with the detection of cells and bacteria utilizing surface-imprinted polymers (SIPs) as whole-cell receptors. Examples will include human cancer cells, CHO cells with membrane modifications, and a variety of bacteria including *E. coli* and *S. aureus*. Special attention will go to the recognition mechanism between cells and SIPs, the selectivity, and enrichment strategies to detect cells at trace levels. In the final part, I will provide an outlook on advanced thermal sensing principles based on thermal waves and the integration of thermal sensing techniques with microbalances and impedimetric sensor readout.

ORAL PRESENTATION

FELIPE CONZUELO

felipe.conzuelo@rub.de

Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-University Bochum

UNRAVELING PHOTOELECTROCHEMICAL PROCESSES AT PHOTOSYSTEM-BASED BIOELECTRODES BY MEANS OF SCANNING PHOTOELECTROCHEMICAL MICROSCOPY

Felipe Conzuelo, Fangyuan Zhao, Volker Hartmann, Marc M. Nowaczyk, Matthias Rögner, Adrian Ruff, Nicolas Plumeré, Wolfgang Schuhmann

The biological photosystems are highly abundant protein complexes involved in the photosynthetic process. They act as photodiodes exciting electrons across the thylakoid membrane upon absorption of visible light. Taking advantage of the high quantum efficiency of these biomolecules, many efforts have been directed to the fabrication of semi-artificial photoelectrochemical assemblies by coupling of isolated redox proteins with different electrode materials. For the development of state-of-the-art devices aiming for a highly efficient performance in solar-to-chemical energy conversion, an extensive evaluation of photoelectrochemical processes occurring at the photobioelectrodes is desired.

We present the use of scanning photoelectrochemical microscopy (SPECM) in the evaluation of bioelectrodes constituted by photosynthetic protein complexes embedded in an Os-complex modified redox polymer [1, 2]. SPECM is a versatile tool for the local assessment of photoelectrochemical processes at the micro scale. By using a tip microelectrode that performs simultaneously as source for local irradiation of the sample and as an electrochemical probe, local photo-electrocatalytic reactions can be easily resolved, allowing a deeper understanding of light-induced electron transfer processes at the semi-artificial assemblies. Examples including the analysis of photosystem-based electrodes under the presence of herbicides and competing charge transfer pathways at the chlorophyll subunits will be shown.

[1] F. Conzuelo, K. Sliozberg, R. Gutkowski, S. Grützke, M. Nebel, W. Schuhmann, Anal. Chem. 89 (2017) 1222–1228.
[2] F. Zhao, N. Plumeré, M.M. Nowaczyk, A. Ruff, W. Schuhmann, F. Conzuelo, Small 13 (2017) 1604093.

Acknowledgements: The authors are grateful to the Cluster of Excellence RESOLV (EXC 1069) and the DIP project “Nanoengineered optobioelectronics with biomaterials and bioinspired assemblies” funded by the DFG for financial support."

MIKHAIL VAGIN

mikva@ifm.liu.se

Laboratory of Organic Electronics, Department of Science and Technology, Linköping University

PROTON AND OXYGEN MANAGEMENT IN CHEMICAL-TO-ELECTRICAL ENERGY INTERCONVERSION ON CONJUGATED POLYMERS

Being one of the main technological inspirations of electrocatalysis, the direct and regenerative fuel cells are employed in a plethora of applications from grid balancing to electrified transport. Among the examples of problematized electrocatalytic processes I would like to consider oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) and direct heterogeneous interconversion of benzenediols. These three examples illustrate the stimulus behind the intensive research on noble-metal-free catalysts.

The hosting of these three processes on the intrinsically conducting polymers (ICP) allows the rational design of catalyst, systematic investigation of mass transport phenomena and mechanistic evaluation of electrocatalysis due to the open material architecture. Firstly, the landscape of ORR phenomena happening on ICP is discussed at the mechanistic and device levels. The effects of co-catalyst and proton supply on ORR efficiency and the pathway is illustrated on the examples of p- and n-type ICP-based ORR catalysts [1-3]. Secondly, the effect of proton supply is rationalized at both mechanistic and device levels for HER on ICP. Thirdly, the crucial effect of proton transport on the rate of benzenediols heterogeneous interconversion is illustrated on ICP-based composites [4]. The establishment of the active proton transport achieved via polymer blending with polyelectrolytes allowed to reach the reversible electron reaction, which might be utilized in future regenerative fuel cells driven by forest fuels.

[1] E. Mitraka, M.J. Jafari, M. Vagin et al., J.Mater.Chem.A 5(9):4404
[2] M. Vagin et al., N-doped conducting polymers for oxygen reduction reaction. Submitted
[3] E. Mitraka, M. Gryszel, M. Vagin et al., Electrocatalytic production of hydrogen peroxide with poly(3,4-ethylenedioxythiophene) electrodes. Submitted
[4] C. Che, M. Vagin et al., Advanced Sustainable Systems, 2018, accepted.

RICHARD BENNETT

r.bennett1@nuigalway.ie

Biomolecular Electronics Research Lab, NUI Galway

ENZYMATIC BIOPOWER: DESIGN OF EXPERIMENT APPROACH FOR OPTIMISATION OF ENZYMATIC ELECTRODES

Richard Bennett, Peter Ó Conghaile, Dónal Leech

Applications of biomedical devices as implantable and semi-implantable systems such as sensors, valves and pumps are of increased importance. These devices rely heavily on battery power which are reliant on re-charging or sufficient reagents contained within. An alternative strategy is fuel cell technology, using readily available in-vivo substrates (glucose and oxygen) as fuel and oxidant. This is difficult to achieve using chemical catalysts as they are non-selective and operate under harsh conditions (pH and temperature). Enzymes as catalysts offer an alternative route towards powering of such devices. Enzymatic active sites are selective and operate under mild conditions thus offering a potential solution for semi-implantable devices.

Here we report on co-immobilization of osmium based redox complexes and support polymers with specific enzymes on electrode surfaces. These enzymes are capable of substrate catalysis (glucose oxidation and oxygen reduction) [1]. Tailoring of the osmium redox potential to the enzyme active site improves electron transfer to electrode surface. Combining enzyme and redox centre with nano supports such as carbon nanotubes achieves higher current densities and greater power outputs. This is achieved through refinement of the immobilisation procedures as well as optimisation of the enzyme electrode components.

Our research uses a design of experiment (DoE) approach for optimisation of electrode surface chemistry to improve current density. The DoE approach improved current density by >50% over traditional one factor at a time (OFAT) approaches, with current densities of 1.2 mA cm^{-2} in biologically relevant glucose concentrations (5 mM) [2].

[1] Ó Conghaile, Peter, et al. Analytical chemistry 88.4 (2016): 2156-2163.
[2] Bennett, Richard, et al. Electroanalysis (2018) Manuscript accepted for publication.

CECILIA CRISTEA

ccristea@umfcluj.ro

Analytical Chemistry Department, "Iuliu Haţieganu" University of Medicine and Pharmacy, Cluj-Napoca

ELECTROCHEMICAL SENSORS FOR SCREENING PSEUDOMONAS AERUGINOSA VIRULENCE FACTORS

Bianca Ciui[1], Mihaela Tertis[1], Andreea Cernat[1], Islem Gandouzi[2], Cecilia Cristea[1]

1 Iuliu Hatieganu University of Medicine and Pharmacy, Faculty of Pharmacy, Department of Analytical Chemistry, 4 Pasteur Street, 400021 Cluj-Napoca, Romania, 2 Laboratory of Analysis, Treatment and Valorisation of the Pollutants of the Environment and Products, Faculty of Pharmacy, University of Monastir, 5000 Avicenne Street, Monastir, Tunisia

Hospital associated nosocomial infections caused by PSEUDOMONAS AERUGINOSA (*P. aeruginosa)* are of interest, being associated with high rates of morbidity and mortality. Siderophores represent important virulence factors for many pathogens, being pathogen-derived molecules utilized in iron acquisition. Thus, their rapid and sensitive detection could be of high importance for the early diagnosis and therapy management of nosocomial infections. The siderophore chosen for our studies was Pyoverdine (PyoV), a mixed-type produced by *P. aeruginosa*, composed of eight amino acids. Pyocianin (PyoC) is another virulence factor related to *P. aeruginosa*, being a zwitterion at blood pH, able to cross the cell membrane. The presence of PyoV and PyoC in water, body fluids or environment can be directly linked to the presence of *Pseudomonas*. These two virulence factors could be electrochemically oxidized with limits of detection in the µM range. Three different approaches were elaborated for the detection of *Pseudomonas* virulence factor detection based on: the deposition of graphene and gold nanoparticles composite film from aqueous suspension; graphene, polypyrrole and gold and finally electrochemically reduced graphene oxide combined with gold nanoparticles, all on the surface of a graphite-based screen-printed electrode. Under optimal conditions, the electrochemical signal corresponding to the PyoV oxidation process was proportional to its concentration, showing a wide linear range from 1 to 100 µM and a detection limit between 0.33 µM to 66.9 nM [1, 2]. All sensors discriminated with satisfactory recoveries the target analyte in different real matrices and exhibited low response to other interfering species, proving that those techniques are promising for possible medical and environmental applications. Finally, a novel glove-embedded printable sensor was designed for simultaneous detection of PyoV and PyoC. Once placed on the hand of a person during an investigation session, the glove-based sensors platform can be used for rapid on-site detection of the targets. The sensors feature linearity from 0.01 to 0.1 µM for PyoC and 5 to 50 µM for PyoV, with a sensitivity of 2.51 µA μM^{-1} for PyoC and 1.09 nA μM^{-1} for PyoV. The main application of the proposed finger-based sensors was the screening of contaminated surfaces such as furniture, medical scrapper, and sink. The integration of the electrochemical sensors in a laboratory glove is expected to inspire modern point-of-care tools used in healthcare to facilitate the prevention of nosocomial infections and to ensure the patient protection.

[1] I. Gandouzi, M. Tertis, A. Cernat, A. Bakhrouf, Maria Coros, S. Pruneanu, C. Cristea, *Bioelectrochem*. 120 (2018) 94–103, [2] A. Cernat, M. Tertis, I. Gandouzi, A. Bakhrouf, M. Suciu, C. Cristea, *Electrochem. Commun.* 88 (2018) 5–9.

Acknowledgments

This work was supported by grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI-UEFISCDI, project number ERANET-RUS-PLUS-PLASMON –ELECTROLIGHT, within PNCDI III.

FEI SHEN

shenfei@kemi.dtu.dk

NanoChemistry Group, Technical University of Denmark

FREESTANDING AND FLEXIBLE GRAPHENE PAPER AS SUPPORT FOR BIOCATALYSTS IN ENZYMATIC BIOFUEL CELLS

Fei Shen, Dmitry Pankratov, Jingdong Zhang, Jens Ulstrup, Qijin Chi

Biocatalysts for enzymatic biofuel cells (EBFCs) require more practicable and spendable electrode materials for accommodation of the enzymes than the traditional solid graphite or expensive noble metal electrodes. We report here the use of novel graphene paper (GP) as a freestanding and flexible cathode and anode electrode material for immobilization of enzymes in a glucose/O_2 EBFC. GP electrodes were prepared via controlled assembly of graphene oxide (GO) nanosheets into a freestanding structure, followed by the specific reduction of GO to reduced GO (rGO). Bilirubin oxidase (BOx) physically adsorbed on the GP electrode, can directly transfer electrons between BOx and the cathode, facilitating the dioxygen reduction reaction (ORR). Likewise, pyrroloquinoline quinone dependent glucose dehydrogenase (PQQ-GDH) was physically immobilized onto a GP anode. However, direct electron transfer between PQQ-GDH and the anode cannot occur because the active site of the enzyme is deeply buried in the protein structure. Meldola blue (MB) was therefore introduced as a mediator shuttling electrons between PQQ-GDH and the anode, and facilitating PQQ-GDH catalysed glucose oxidation. As a result, an EBFC with a robust open circuit voltage up to 0.625 V and max power density of 3.97 μW/cm^2 could be obtained. These values are competitive with established EBFCs. The new GP supported EBFC holds potential for operating under in vivo conditions, e.g. integrated in biological compartments, and driving a low-power device such as a pacemaker.

ROBERT CRAPNELL

r.crapnell@mmu.ac.uk

Peeters research group, Manchester Metropolitan University

DEVELOPMENT OF A FLEXIBLE MIP-BASED BIOSENSOR PLATFORM FOR THE THERMAL DETECTION OF BIOMOLECULES

R. Crapnell, M. Peeters, K. Betlem, C.W. Foster, M. Down, K. Eersels, B. van Grinsven, T.J. Cleij, C.E. Banks

Molecularly Imprinted Polymers (MIPs) are synthetic antibody mimics; similar to antibodies, they have high affinity for a chosen template molecule but their advantages include low-cost, superior chemical and thermal stability, and straightforward production process. In this contribution, MIP particles are mixed with screen-printed ink to produce mass-producible bulk modified MIP Screen-Printed Electrode (MIP-SPEs). We will explore different SPE supporting surfaces, including polyester, tracing paper and household-printing paper [1].The performance of these MIP-SPEs is studied with cyclic voltammetry and two (patented) thermal techniques, including the Heat-Transfer Method (HTM) and Thermal Wave Transport Analysis. Advantages of these thermal techniques include that they are label-free, low-cost and data processing is straightforward. The thermal response through the MIP-SPEs is determined by measuring the temperature gradient between the sensor surface and liquid.

Sensors printed onto household-printing paper were considered in further experiments as they exhibited the highest thermal and electrical response to in addition to advantageous material properties, including sustainability and flexibility of the material. TWTA, a thermal method that was first introduced in 2016, was proven to be a promising alternative compared to HTM as it had a shorter measurement time (2 min) and significantly higher signal to noise ratio. In recent work, the technique has been further exploited to determine the presence of pathogenic bacteria [2], growth of microorganisms and evaluation of enzyme catalysis. A sensor platform has been designed that is flexible and portable; therefore, it holds great potential for the use in biomedical devices and complex sensor architectures.

[1] S. Casadio, et al., Chem. Eng. J. 2017, 315, 459.
[2] E. SteenRedeker et al., ACS Inf. Dis. 2017, 3, 388.

ALEXANDRA VERHAVEN

averhave@ulb.ac.be

CHANI, Université libre de Bruxelles

STUDY OF DNA SINGLE NUCLEOTIDE POLYMORPHISM BY ELECTROCHEMICAL IN SITU FLUORESCENCE MICROSCOPY

Alexandra Verhaven, Dan Bizzotto, Thomas Doneux

The detection of single nucleotide polymorphisms (SNPs) in DNA is of utmost importance as SNPs are associated with various human diseases.

In this work, we investigate a detection methodology based on the electric-field assisted denaturation of DNA. The employed technique couples electrochemical measurements with in situ fluorescence microscopy in real time. Electrochemistry is used to induce the denaturation of DNA, while fluorescence measurements are employed to detect the associated melting events. For this purpose, fluorescently labelled DNA sequences are immobilized at gold electrodes as self-assembled monolayers (SAMs), the probe being thiolated and the complementary strand bearing a fluorescent label, in both instances at the 5'- extremity.

We present the results of a comparative study of perfect match and SNP-containing target sequences (e.g. SNP 309T>G of the human MDM2 gene). The presence of a mismatch in a sequence significantly reduces the stability of the DNA duplex, therefore making it more susceptible to electric-field induced denaturation. Because the fluorescence is heavily quenched by the bulk metal electrode, in a distance-dependent way, the denaturation and subsequent desorption of the double-strand both give rise to strong fluorescence bursts when the potential is swept in the negative direction.

The potential induced melting of the DNA is significantly influenced by the assembly of the SAM. We present the influence of various parameters, such as the nature of the probe (linear vs. hairpin DNA), nature of the diluent (mercaptohexanol vs. mercaptobutanol) and surface coverage. We also show the influence of the measurement conditions such as the ionic strength of the measurement buffer and time.

Finally, we present our findings concerning a FRET-based labelling strategy. The FRET process was studied for fluorophore tagged DNA SAMs with different acceptor/donor ratios.

XU ZHANG

Xu.Zhang@UGent.be

Centre for Microbial Ecology and Technology, Ghent University

PERIODIC POLARIZATION OF ELECTROACTIVE BIOFILMS INCREASES CURRENT DENSITY AND CHARGE CARRIERS CONCENTRATION WHILE MODIFYING BIOFILM STRUCTURE

Xu Zhang, Antonin Prévoteau, Korneel Rabaey

Anodic electroactive biofilms (EABs) have been considered promising for several potential applications such as microbial fuel cells, microbial electrolysis cells or microbial biosensors. However, low current densities still limit their practicability and numerous questions remain on the parameters impacting their characteristics and performance. EABs are able to store electrons in the absence of external electron acceptor ("charge" process in open circuit). Once the microbial anode is polarized again, accumulated charges can be released and it produces an additional transient current ("discharge" process). This process has already been studied but solely for short-term and on already mature EABs. In particular, the effect of periodic polarization on the properties of the EABs has not been explored.

Here we applied periodic polarization (i.e. alternating half periods at open circuit and half periods at – 0.1 V vs. Ag/AgCl) during the full growth of EABs on glassy carbon electrodes (i.e. starting from inoculation). We investigated the impact of the frequency of the signal on current generation, charge storage capacity, heme content, apparent redox conduction and biofilm morphology.

When compared with a continuous polarization, the shortest half-periods of charge/discharge (≤ 10 s) enhanced current production, increased the content of redox cofactors (and hemes) in the EABs, and improved the apparent redox conduction. Oppositely, longer half-periods (≥ 60 s) inhibited the growth and electroactivity of the EABs. Control EABs formed under continuous polarization were flat, while EABs formed under intermittent operation presented mushroom-shaped structures on their outer-layer. The results indicated that periodic polarization can regulate the formation and electroactivity of EABs. In addition to the fundamental relevance, this electrochemical optimization may provide opportunities for future applications.

ANTONIN PRÉVOTEAU

Antonin.Prevoteau@Ugent.be

Center for Microbial Ecology and Technology, Ghent University

AN OXYGEN REDUCING MICROBIAL CATHODE MONITORING TOXIC COMPOUNDS IN FRESHWATER

Antonin Prévoteau, Peter Clauwaert, Frederiek-Maarten Kerckhof, Korneel Rabaey

Electroactive biofilms (EABs) have recently spiked considerable research interest for their putative use as amperometric biosensors in environmental or bioprocess monitoring. They are attractive because of their low cost, fast and easy signal transduction and their self-regenerative properties. Among other putative sensing applications, EABs could be used for early in situ detection of toxic compounds since the current generated is directly dependent on the microbial activity. Almost all related studies have investigated heterotrophic, anodic EABs whose microbial community is typically dominated by the 'ubiquitous' *Geobacter spp*. However, these EABs require the presence of an organic substrate (as electron donor and carbon source) along with local anaerobic conditions to deliver current, which obviously limits the range of applications.

Here we present an investigation of 'electroautotrophic', O_2-reducing EABs grown on graphite rods at + 0.2 V vs. Ag/AgCl. The voltammograms of these microbial cathodes showed a reproducible nernstian behavior with high onset (+ 0.42 V) and mid-point (+ 0.3 V) potentials for O_2 reduction, and plateau current densities of ~ 80 µA.cm^{-2}, at pH 7.2. The microbial communities of the EABs were dominated by an unclassified representative of the γ-proteobacteria, as was observed in previous studies of O_2-reducing EABs.

The microbial community only required O_2 and very limited amount of nutrients to be metabolically active, allowing a continuous production of microbial current in tap water at + 0.1 V vs. Ag/AgCl. These biocathodes could non-specifically monitor the addition of toxic compounds, and were typically more sensitive than anodic EAB towards these toxic shocks. These cheap and simple early warning biosensors could allow immediate decision-making in places where other complex analytical techniques are seldom available on site, such as remote areas or developing countries.

BIANCA CIUI

ciuibianca@yahoo.com

Analytical Chemistry Department, Iuliu Haţieganu University of Medicine and Pharmacy Cluj-Napoca

PRINTED ELECTROCHEMICAL SENSORS FOR HEALTH AND ENVIRONMENTAL APPLICATION

Bianca Ciui, Aida Martin, Rupesh K. Mishra, Mihaela Tertiş , Robert Săndulescu , Joseph Wang, Cecilia Cristea

Recent advancement in approaches of electrochemical techniques and their novel applications in the design of wearable chemical sensors have added rich, analytical information to the wearer in a timely manner. Wearable electrochemical sensors have been integrated onto textile materials or directly on to the skin for diverse range of applications. Besides, wearable sensors received considerable interest owing to their promise for monitoring threat compounds in an individual surrounding [1].

One example of wearable sensor is based on screen printing conductive inks on a medical bandage for non-invasive screening of skin melanoma. The wearable electrochemical bandage sensor was capable of detecting the presence of the tyrosinase (TYR), a cancer biomarker, in the presence of its catechol substrate, immobilized on the transducer surface. The analytical performance of the resulting bandage sensing systems was evaluated using TYR-containing agarose phantom gel and porcine skin [2].

Hospital-associated nosocomial infections caused by *Pseudomonas aeruginosa* (P. aeruginosa) and its virulence factors, are of particular interest, being associated with high rates of morbidity and mortality. These compounds colonize moist environments and damp places such as sinks, furniture and medical equipment. Based on the demand for early 'on-site' detection of *P. aeruginosa* and its virulence factors, a glove-based electrochemical sensor has been designed for screening of relevant contaminated surfaces [3].

Saliva is a valuable source of biochemical information accessible in a non-invasive manner. N(6)-carboxymethyllysine (CML), is an advanced glycation end-product, affecting nearly every type of cell and molecule in the body and is thought to be a factor in aging and some age-related chronic disease. An electrochemical sensor mounted on a mouth-guard was designed for non-invasive monitoring of CML, with great outcomes regarding the analysis in real sample [4].

[1] A. J. Bandodkar, I. Jeerapan, J. Wang, ACS Sensors, 2016.
[2] B. Ciui, A. Martin, R. K. Mishra, B. Brunetti, T. Nakagawa, T. J. Dawkins, M. Lyu, C. Cristea, R. Săndulescu, J. Wang, Adv. Healthc. Mater., 2018.
[3] B. Ciui, M, Tertiş, A. Cernat, R. Săndulescu, J. Wang, C. Cristea, Anal. Chem., 2018.
[4] B. Ciui, M, Tertiş, C. Feurdean, A. Ilea, R. Săndulescu, J. Wang, C. Cristea, submitted

ANNA BANASIAK

d14126212@mydit.ie

Applied Electrochemistry Group, Dublin Institute of Technology

STUDYING THE MODE OF INTERACTION AND DNA NUCLEASE EFFICACY OF NOVEL BIOINORGANIC COMPOUNDS USING ELECTROCHEMICAL DNA BIOSENSORS

Anna Banasiak, John Cassidy, John Colleran

Some bioinorganic compounds (BC), during interaction with DNA, can change the conformation of DNA and block binding sites. Additionally, some BC can promote a Fenton-like reaction that leads to the creation of reactive oxygen and nitrogen species. DNA-BC interaction can inhibit DNA replication and, consequently, result in cell death. Hence, some BC have the potential to be used as anticancer drugs as they can efficiently kill cancer cells.

The aim of this research project is to use electrochemical DNA biosensors to investigate the interactions between DNA and BC, in particular, focusing on the nuclease activity of BC. The DNA sensors were fabricated through chemisorption of thiol-modified double-stranded DNA oligonucleotides to create a self-assembled monolayer (SAM) on the gold electrode surface.

The DNA sensors were immersed in solutions containing the BC of choice. The redox profile of BC can be observed at the bare gold and DNA sensor. The observed redox behaviour of the BC is facilitated by the DNA strand via a long-range electron transfer mechanism – stacked DNA base pairs behave as the electron conduit between the gold surface and the BC bound to the DNA layer. Comparison of the BC redox waves at the bare and DNA modified electrode can reveal information about the type of binding mechanism.

The DNA cleavage can be induced chemically, using a Fenton-like nuclease assay containing the BC of choice, an oxidant and a reductant. The nuclease activity of several BC is investigated through the measurement of changes in the DNA electrode surface coverage before and after interaction with the BC nuclease assay. DNA nuclease efficacy can be reported as a percentage of the amount of DNA cleaved from the DNA-SAM.

JERZY RADECKI

j.radecki@pan.olsztyn.pl

Department of Biosensors, Institute of Animal Reproduction and Food Research, Polish Academy of Sciences

REDOX ACTIVE MONOLAYERS FOR EXPLORING OF ANION RECOGNITIONS PROCESSES IN AQUEOUS PHASE

In recent decade, the intermolecular recognition of anions in water has been attracted the attention of numerous scientific groups involved in supramolecular chemistry [1, 2]. The most of literature reports the recognition of anions in one organic phase. Developing systems for the recognition of anions in water medium is still a challenging task. Here, we proposed the dipyrromethene modified with dipodal anion receptor [3] or cyclopeptide attached to electrochemically active dipyrromethene-Cu(II) complex or dipyrromethene-Co(II) complex deposited on the surface of gold electrodes. The developed systems were characterized electrochemically using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV), atomic force microscope (AFM) and contact angle measurements (OCA). Then, modified electrodes were successfully applied for the electrochemical recognition of anions in highly diluted aqueous medium (in the picomolar range). The results obtained allowed establishing the mechanism of communication between the redox centre and receptor anion complex as well as analytical signal generation.

[1] M.J. Langton, C.J. Serpell, P.D. Beer, Angew. Chem. Int. Ed. 55 (2016) 1974.
[2] S. Kubik, Chem. Soc. Rev. 39 (2010) 3648.
[3] B. Kaur, C.A. Erdamnn, M. Daniels, W. Dehaen, Z. Rafiński, H. Radecka , J. Radecki, Anal. Chem. 2017, 89, 12756-12763.

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

PETER CORNELIS

peter.cornelis@kuleuven.be

Soft-Matter Physics and Biophysics Section (ZMB), KULeuven

OPTIMIZING THE HEAT TRANSFER METHOD: LOWERING THE DETECTION LIMITS

P. Cornelis, H. Iken, M. J. Schöning, P. Wagner

Recently the Heat Transfer Method (HTM) established itself as a low-cost alternative in various bio-analytical fields. Its working principle is based on detecting changes in the thermal conductivity at the solid-liquid interface. However, in its original design it is susceptible to parasitic heat losses to the environment. A redesigned setup around a new controllable heat source no longer has this limitation. Therefore, as an example, it was able to lower the detection limit from $1E^4$ CFU/ml to significantly below $1E^3$ CFU/ml.

JULIAN SZCZESNY

julian.szczesny@rub.de

Analytische Chemie - Elektroanalytik & Sensorik, Prof. Dr. Wolfgang Schuhmann, Ruhr-Universität Bochum

A HIGH-PERFORMANCE GAS BREATHING H_2/O_2 BIOFUEL CELLS COMPRISING A HYDROGENASE/POLYMER BASED BIOANODE

Julian Szczesny[a], Nikola Marković[a] Felipe Conzuelo[a], Sónia Zacarias[b], Inês C. Pereira[b], Wolfgang Lubitz[c], Nicolas Plumeré[d], Adrian Ruff[a], Wolfgang Schuhmann[a]

a Analytical Chemistry – Elektroanalytik und Sensorik, 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 Max-Planck-Institut für Chemische Energiekonversion, Stiftstrasse 34-36, D-45470, Mülheim, Ruhr, Germany.
d Center for Electrochemical Sciences (CES) – Molecular Nanostructures, Ruhr-Universität Bochum, D-44870 Bochum, Germany.

Limitations in the use of hydrogenases for energy conversion systems, e.g. the deactivation by O_2 and at high potentials could already be overcome by the incorporation of these enzymes into redox active hydro-gels exhibiting low potentials and thus being able to reduce O_2 while simultaneously acting as a Nernst buffer for the redox protein.

For H_2/O_2 fuel cells based on a rather conventional design, the sufficient supply of gaseous substrates e.g. H_2 and O_2 typically is the rate limiting step due to their low solubility in aqueous media. Hence, the fabrication of high performance bioelectrochemical devices is still a major challenge. The use of gas diffusion bioelectrodes is a promising approach to overcome substrate diffusion limitation in bioelectrocatalysis. These electrodes exhibit a three-phase interphase and thus high local substrate concentrations at the active sites. Moreover, they provide a good conductivity, balance of hydrophobicity and hydrophilicity to offer a suitable environment for the enzyme but can still prevent aqueous solutions from leaking. Furthermore, a high gas permeability is granted to allow for high concentrations of gaseous substrates at the catalyst location under passive conditions.

Combining the benefits of redox polymer/enzyme electrodes, e.g. protection from O_2 and high potential deactivation, with the concept of a gas diffusion electrode additionally allows for high substrate concentrations at the active site of the electrodes and thus, high currents which are desired for the fabrication of high current bioelectrodes.

Here, we present a gas breathing H_2/O_2 biofuel cell with a H_2 oxidizing bioanode based on redox polymers in combination with hydrogenases and an O_2 reducing, bilirubin oxidase-based biocathode. For the biofuel cell, an open circuit voltage of 1.13 V and a power output of 3.6 mW/cm² at 0.7 V was obtained, which sets a benchmark for redox polymer/hydrogenase containing biofuel cells.

HANNA RADECKA

h.radecka@pan.olsztyn.pl

Laboratory of Bioelectroanalysis, Institute of Animal Reproduction and Food Research, Polish Academy of Sciences

ELECTROCHEMICAL IMMUNOSENSORS –ANALYTICAL TOOLS BETTER THEN ELISA?

The naturally high selectivity and efficiency of pathogens - antibodies binding make immunosensors very promising analytical tools.

Here, we report examples of successful developing of several type of immunosensors. The immunosensor were developed by the successive modification of gold [1-2] as well as glassy carbon electrodes [3]. The whole antibody or their fragments have been applied as the sensing elements. The complex between antigens 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, was monitored by the electrochemical impedance spectroscopy (EIS) in the presence of redox marker. Another type of immunosensors is based on redox active layers incorporated di-pyrromethene-Cu(II) [4-7]. The changes of electrochemical parameters of redox centres upon target analyte binging are the base of analytical signal generation.

The both type of immunosensors displayed better sensitivity towards antigens as well as antibodies in the comparison to ELISA. They are also very selective. The complex matrixes have no influence on the immunosensors performance. In addition, very small analysed sample volume (10 µl) is needed. After miniaturisation, they keep excellent analytical parameters [8].

Therefore, immunosensors presented could be recommended for the direct electrochemical detection of antigens as well as antibodies in the natural physiological samples.

[1] Biosensors and Bioelectronics, 24, 2008, 284-289
[2] Biosensors & Bioelectronics, 2014, 55,301-306;
[3] Electroanalysis 2013, 25, 433
[4] Analytical & Bioanalytical Chemistry, Anal Bioanal Chem (2015) 407:7807-7814
[5] Current Alzheimer Research 2017, 14(3): 345-351
[6] Sensors 2013, 13(9): 11586-11602
[7] Sensors 2014, 14(6): 10650-10663
[8] Sensors & Actuators B: Chemical 228 (2016) 25-30.

LISELOTTE NEVEN

Liselotte.Neven@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

PHOTOELECTROCHEMICAL DETECTION OF PHENOLIC ANTIBIOTICS

Liselotte Neven, Nick Sleegers, Stanislav Trashin, Karolien De Wael

The mass production and misuse of antibiotics and the exposure in waste streams result in the natural evolution of bacteria causing them to mutate. This antibiotics resistance reduces the effectiveness of our drugs and is therefore one of the major health problems concerning our society. Therefore the rapid detection of these antibiotics is of crucial importance. A common detection strategy for antibiotics is liquid chromatography coupled with mass spectrometry. It is however traditionally performed in the lab and requires skilled persons. The Delvotest® on the other hand is used for on-site detection but can take up to 2-3 hours for each test.

Therefore we propose the use of a fast and robust photoelectrochemical sensor. It uses a photosensitizer type II which generates singlet oxygen upon light illumination. Singlet oxygen and/or secondary formed redox species result in a current response due to the reduction of these species at the electrode surface. The catalytic conversion of phenolic compounds, mediated by singlet oxygen, leads to an improved sensitivity and lower detection limits (nM-level). The proposed detection strategy possesses an intrinsic background illumination feature by switching the laser on and off [1].

To demonstrate the use of the proposed photoelectrochemical sensor for the detection of antibiotics, the detection of cefadroxil (a β-lactam antibiotic) and doxycycline (a tetracycline antibiotic) was optimized. Through the use of linear sweep voltammetry together with amperometric measurements, an optimal pH and potential was determined. With these optimized conditions a calibration curve was made so that based on the slope a LOD and LOQ was determined. Interestingly a different photoresponse was obtained for each of these antibiotics presumably due to their structural differences. As a consequence different oxidized products were formed which resulted in different kinetics at the electrode surface.

[1] Trashin, S., et al. Nat Comm, 2017, 8.

MATHIEU ETIENNE

mathieu.etienne@univ-lorraine.fr

LCPME, CNRS, Université de Lorraine

ELABORATION AND CHARACTERIZATION OF LIVING BIOCOMPOSITE ELECTRODES

Mathieu Etienne, Stéphane Pinck, Frédéric Jorand, Elisabeth Lojou

A living material was formed by self-assembly of *Shewanella oneidensis* MR-1 with carbon nanotubes in the presence of c-type cytochrome from *Desulfovibrio* and *Desulfuromonas* genus and from bovine heart, with the goal to mimic electroactive biofilms [1]. The role of cytochromes on self-assembly, cell viability and extracellular electron transfer was studied for formate oxidation and fumarate reduction. Scanning electron microscopy and dynamic light scattering experiments highlighted the role of cytochrome on the self-assembly of bacteria-carbon nanotube aggregates within only two hours in solution. The deposition of these aggregates on glassy carbon surfaces led to a homogeneous composite film in which the bacteria were embedded in a carbon nanotube network. A comparable cell density of one cell µm-2 was achieved in the presence or in the absence of cytochrome c, but cytochrome allowed maintaining a higher bacterial viability [2]. Finally, this electroactive artificial biofilm can be used to study the mechanisms of electron transfer in electroactive biofilms, as it will be discussed with selected illustrations.

[1] S. Pinck, F. Jorand, M. Etienne, Electrochemistry of Biofilms, in: Ref. Modul. Chem. Mol. Sci. Chem. Eng., Elsevier, 2017

[2] S. Pinck, M. Etienne, M. Dossot, F.P.A. Jorand, A rapid and simple protocol to prepare a living biocomposite that mimics electroactive biofilms, Bioelectrochemistry. 118 (2017) 131–138

CHERYL KARMAN

cheryl.karman@uantwerpen.be

ECOBE and AXES research group, Department of Chemistry, University of Antwerp

UNDERSTANDING THE ELECTRON TRANSFER MECHANISM OF CABLE BACTERIA

Cheryl Karman[a, b], Karolien De Wael[a], Filip J.R. Meysman[b]

[a] AXES Research group, Department of Chemistry, University of Antwerp, [b] ECOBE Research group, Department of Biology, University of Antwerp.

In 2012, Pfeffer *et al* reported the discovery of a novel type of filamentous sulphur oxidizing bacteria belonging to the Desulfobulbaceae family.[1] The so-called 'cable bacteria' can perform long-distance electron transfer (LDET) across centimeter scales in aquatic sediments.[2] The metabolic activity of these electroactive microorganisms is indicated by a characteristic pH depth profile in the sediment, where the pH is higher (pH 8.5) in the narrow oxic zone at the surface and lower (pH 6.5) in deeper anoxic layers of the sediment.[3] This pH depth profile is generated by the spatial separation of two redox half-reactions: proton production from sulfide oxidation in deeper layer and proton consumption by oxygen reduction in the upper oxic layer. In our research groups, we investigate the chemical composition, morphology and electrochemical properties of cable bacteria cell envelope, in order to better understand the mechanism of the long-distance electron transfer. An important challenging question is how electrons are transported from cell to cell inside the cable bacterium filaments a (intracellular transfer) as well as between the cable bacteria and their surroundings (extracellular electron transfer; EET).[4] The latter is the main objective of our study, where we deposit cable bacteria filaments on a gold electrode surface and study the electron transfer of possible redox active biomolecules (e.g. cytochromes, as reported recently[5]) in cable bacteria. Preliminary results indicated the presence of redox active species on the surface of cable bacteria as well as its catalytic activity towards oxygen. Studies incorporating enzyme inhibitors and redox mediators in the experimental media are expected to help us understand better the biomolecules participating in the EET, in parallel with the proteomics analysis that are currently conducted. A spectro-electrochemical study, coupling voltammetric technique with Raman spectroscopy will be done to further support the obtained results, by direct correlation between the protein redox states and the Raman spectra evolutions.

1. Pfeffer, C. et al. Filamentous bacteria transport electrons over centimetre distances. Nature 491, 218–221 (2012).
2. Burdorf, L. D. W. et al. Long-distance electron transport occurs globally in marine sediments. Biogeosciences 14, 683–701 (2017).
3. Meysman, F. J. R., et al. The geochemical fingerprint of microbial long-distance electron transport in the seafloor. Geochim. Cosmochim. Acta 152, 122–142 (2015).
4. Meysman, F. J. R. Cable Bacteria Take a New Breath Using Long-Distance Electricity. Trends Microbiol. 26, 411–422 (2018).
5. Bjerg, J. T. et al. Long-distance electron transport in individual, living cable bacteria. Proc. Natl. Acad. Sci. 1–6 (2018).

MIHIR GUPTA

mihir.gupta@imec.be

Department of Physics and Astronomy (KU Leuven) and Life Science Technologies (imec)

PH SENSING USING NANO-SCALED CMOS COMPATIBLE FInFETs

M. Gupta, A. Veloso, Z. Tao, W. Li, L. Lagae, K. Martens, W. Van Roy

ISFETs have been fabricated using a variety of technologies, including carbon nanotubes [1], Si nanowires [2], Si bulk and Silicon on Insulator (SOI) FinFETs [3]. For integration into applications like Lab-on-Chip, a CMOS compatible technology is preferred. Here we report FinFETs fabricated on 300 mm SOI wafers with 30 nm thick Si layer, for a range of widths (15 nm to 1 µm) and lengths (250 nm to 10 µm) patterned using 193 nm immersion lithography. The gate oxide stack consists of 3 nm SiON layer and 1 nm ALD SiO_2. The devices we report here, to our knowledge, are the narrowest CMOS compatible FinFETs used as ISFETs for pH sensing.

The pH measurements were performed in 10 mM buffer ranging from pH 3 to pH 10. The choice of the reference electrode for gating is very important, hence we analysed different reference electrodes that are typically used for ISFET applications. We observed parasitics associated with using Au or pseudo Ag/AgCl as reference electrode, and found that a true Ag/AgCl electrode is the preferred choice.

We have also analysed the choice of gate oxide in contact with the electrolyte. In literature sensitivities of 30mV/pH for SiO_2 [3] and 58mV/pH for Ta_2O_5 [4] have been obtained. Our analysis agrees with literature and shows 30-40 mV/pH for SiO_2 surface and 50-58 mV/pH for Ta_2O_5 surface.

In literature there is no consensus on the FET width dependence for pH sensing, where some papers claim that there is a dependence while some do not [5][6]. We conducted various experiments to try to understand if and by what factor does pH sensing depend on the geometry of the FinFETs, and we will discuss this in the meeting.

[1] Cid, et al., Analyst, 133.8 (2008) :1001-1004
[2] Huang, et al., IEEE Sensors Journal (2017)
[3] Rigante, et al., ACS nano 9.5 (2015) :4872-4881
[4] Mikolajick, et al., Sens. Actuators B Chem. 44, 262–267(1997)
[5] Elfström, et al., Nano Letters 7.9:2608-2612 (2007)
[6] Bedner, et al., Sensors and Materials 25.EPFL-ARTICLE-195358 (2013):567-576

RUI CAMPOS

rui.acampos@gmail.com

AXES Research group, Department of Chemistry, University of Antwerp, INL-International Iberian Nanotechnology Laboratory, iNANO-Interdisciplinary Nanoscience Centre

ELECTROCHEMISTRY APPLIED TO GENOSENSOR DEVELOPMENT

R. Campos, E. Farjami, I. Álvarez-Martos, J. S. Nielsen, K. V. Gothelf, J. Kjems, E. E. Ferapontova, G. Machado Jr, M.F. Cerqueira, J. Borme and P. Alpuim

Nucleic acids are attractive and open a wide range of possibilities when it comes to biosensor development. A DNA or RNA strand can be used to detect its complementary sequence, small molecules or proteins. In the case of complementary strand detection the sensor should be sensitive to single nucleotide polymorphisms, which is highly important for health related applications. In contrast, for small molecule detection the ability to distinguish the molecule of interest from its interferents is crucial.

Electrochemistry is a powerful tool that together with nucleic acids allows the development of highly sensitive genosensors. Here two different applications of the genosensor will be discussed: i) the detection of dopamine, a small molecule involved in various diseases, and ii) the detection of a DNA strand using a graphene microelectrode array.

For the detection of dopamine a genosensor was developed based on its RNA aptamer. Specific recognition of this target by the aptamer allowed a selective amperometric detection within the relevant physiologically range – 100 nM to 5 µM – in the presence of competitive concentrations of interferents. [1, 2]

As for the detection of DNA hybridization, electrochemical chips consisting of 6 independent transferred graphene microelectrode arrays were used. The sensitivity of electrochemical impedance spectroscopy together with the selectivity of DNA beacons, allowed DNA hybridization to be detected in a linear range between 5 pM and 5 nM. Importantly, this is within the relevant clinical range for many diseases and presents sensitivity to single nucleotide polymorphisms. [3]

[1] Farjami, E.; Campos, R.; Nielsen, J. S.; Gothelf, K. V.; Kjems, J.; Ferapontova, E. E, Anal. Chem. 2013, 85 (1), 121–128.
[2] Álvarez-Martos, I.; Campos, R.; Ferapontova, E. E, Analyst 2015, 140 (12), 4089–4096.
[3] Campos, R.; Machado, G.; Cerqueira, M. F.; Borme, J.; Alpuim, P. , Microelectron. Eng. 2018, 189, 85–90

PAULA LOPES

paula.lopes@ugent.be

CMST - Centre for Microsystems Technology, Gent University

A PROTEIN-BASED ELECTROCHEMICAL BIOSENSOR FOR FACILE AND SENSITIVE DETECTION OF OSTEOPOROSIS BIOMARKERS

Paula Lopes [1], Patricia Khashayar [1], Mieke Adriaens [2], Jan Vanfleteren [1]

1-Center for Microsystems Technology (CMST), Ghent University and IMEC, Technologiepark 15, 9052 Gent-Zwijnaarde, Belgium;
2-Department of Chemistry, Ghent University, Krijgslaan 281 S12, 9000 Gent, Belgium

Bone loss and osteoporosis is a serious health problem worldwide. Statistically, 33% of women and 20% men over 50 years of age will experience osteoporotic fractures in their life [1]. This reality represents an enormous burden on healthcare systems worldwide and highlights the critical need to improve early diagnosis of bone loss and the development of rapid and inexpensive detection systems as well as treatment monitoring.

At present, electrochemical biosensors are widely used in medical practice, as they offer extremely sensitive and accurate yet simple, rapid, and inexpensive biosensing platforms for diagnosis. In this context, we are developing a proteomic sensor, to be integrated in a point-of-care device, for bone turnover markers (BTMs) detection [2]. The development of a label-free biosensor for the detection of C-terminal telopeptide from type-1 collagen (CTx-I), will be discussed.

Sulfo-LC-SPDP cross-linker and anti-CTx-I antibody are mixed and immobilized on the electrode surface thereafter. Nonspecific interactions are prevented by using BSA as a passivating agent. The sensing layer is prepared using a gold screen printed electrode and characterized using differential pulse voltammetry and electrochemical impedance spectroscopy. Optimization studies have shown successful detection of CTx-I within the relevant clinical range, 100-2500 pg mL^{-1}.

This sensor can be extended to other BTMs in a multiplex detection system with the potential to constitute a breakthrough in the current medical care settings of osteoporotic patients, by contributing to an early diagnosis and screening of the disease.

[1] Hernlund, E., et al. Arch Osteoporos (2013) 8:136
[2] Khashayar, P., et al., Micromachines (2017) 8:133

The work is funded by the European Commission in the framework of the H2020-NMBP-X-KET-2017- “PoCOsteo” Research & Innovation Action (Grant Agreement number 767325) and is supported and advised by the International Osteoporosis Foundation (IOF).

GIDEON WACKERS

gideon.wackers@kuleuven.be

Soft-matter physics and biophysics section (ZMB), KULeuven

A MEDICAL CATHETER FOR GASTRO-INTESTINAL HISTAMINE DETECTION

Wackers G., Putzeys T., Verhaert N., Wübbenhorst M., Peeters M., Wagner P.

Titanium wires were functionalized with Molecularly Imprinted Polymers in order to construct a catheter for the in-patient detection of histamine in the gastrointestinal tract. Besides the shift from planar substrates to coated wires, a new data extraction method is described, which allows improved sensor responses down to the nanomolar range.

GIULIA MORO

gmoro93@gmail.com

LSE Research Group, Department of Molecular Science and Nanosystems, Ca' Foscari University of Venice

CONDUCTIVE IMPRINTED POLYMERS FOR THE DIRECT ELECTROCHEMICAL DETECTION OF B-LACTAM ANTIBIOTICS: THE CASE OF CEFQUINOME

Giulia Moro[a], Anca Florea[b], Fabio Bottari[b], Karolien De Wael[b], Ligia Maria Moretto[a]

[a] LSE Research Group, Department of Molecular Science and Nanosystems, Ca' Foscari University of Venice

[b] AXES Research group, Department of Chemistry, University of Antwerp

Biomimetic materials, such as molecularly imprinted polymers (MIPs), answer perfectly the demand of tuneable electrode modifiers, required for the design of electrochemical biomimetic sensors for the selective detection of emerging contaminants, such as β-lactam antibiotics. MIPs can be directly integrated with the electrode surface by electropolymerization. If the electropolymerization gives rise to conductive polymers a direct electrochemical detection of an electroactive analyte should be possible. The selectivity provided by the key-lock mechanism of MIPs cavities will add up to the specific electrochemical signal of the target leading to highly selective sensors.

As a proof-of-concept for the realisation of a biomimetic sensor array for β-lactam detection in milk, a MIP-sensor for cefquinome (CFQ) detection was designed. CFQ is a fourth generation cephalosporin with a specific electrochemical signal related to its 2-amino-5-thyazolyl acetamido substituent. The selection of the monomer for CFQ-MIPs, namely 4-aminobenzoic acid (4-ABA), was based on a rational design screening of electropolymerizable monomers performed with Sybyl 7.3 software package. A broad electropolymerization study was carried out to map the pH-dependence in relation to the electrochemical properties: conductive poly(4-ABA) can be obtained at pH 1 and 7, while for intermediate pH values the polymer results to be isolating. Aiming to exploit a direct electrochemical detection, CFQ MIPs were synthesized by electropolymerization at pH 1 (0.1 M sulphuric acid) performing seven consecutive voltammetric cycles (scan rate 50 mV/s), with a monomer:target ratio of 5:1 on multi-walled carbon nanotubes graphite screen printed electrodes. Under optimum conditions, the lower cefquinome concentration detectable on the modified electrodes was 50 nM in 0.1 M PB pH 2, not far away from the CFQ maximum residue limit in milk of 38 nM established by the EU.

LIGIA MORETTO

moretto@unive.it

LSE Research Group, Department of Molecular Science and Nanosystems, Ca' Foscari University of Venice

ELECTROCHEMICAL SENSOR BASED ON MOLECULARLY IMPRINTED POLYMER FOR TRACE PERFLUOROOCTANE SULFONATE ANALYSIS IN ENVIRONMENTAL SAMPLES

Ligia Maria Moretto, Najmeh Karimian, Angela Maria Stortini, Paolo Ugo

Perfluoroalkyl substances (PFAS) is a wide group of man-made chemicals largely employed in industry and consumers products. Contamination of water by PFAS is a problem of global concern due to its suspected toxicity and bioaccumulation [1]. Perfluorooctane sulfonate (PFOS) is the perfluorinated compound of major concern. Molecular imprinting technology as a promising alternative approach, offers interesting characteristics such as cost effectiveness, stability, sensitivity, selectivity, able to easily perform the rapid determination to furnish recognition systems in the field of (bio)sensors.

Molecularly imprinted polymer (MIP) - coated electrodes are prepared by the formation of a polymer network around a template. The electrosynthetic approach simply and rapidly creates an adherent and compact polymeric film with controllable thickness, which could be very helpful both in improving the molecular imprinting polymerisation procedure and in extending the application of MIPs [2, 3]. In this communication, the fabrication and characterization of a novel electrochemical sensor for sensitive and selective detection of PFOS based on a molecularly-imprinted electrosynthesised polymer is reported. A PFOS sensitive layer was prepared by electropolymerization of o-phenylenediamine (o-PD) on a gold electrode in the presence of PFOS as template. To develop the MIP the template molecules were removed from the modified electrode surface with suitable solvent mixture. The processes of electropolymerization, template removal and binding of the analyte, were followed by voltammetry, quartz crystal microbalance and SEM-EDX. The incubation of the MIP-modified electrode with respect to PFOS concentration resulted in a suppression of the Ferrocenecarboxylic acid (FcCOOH) probe signal. The sensor was successfully tested for analysing PFOS in water at 0.1 nM - 1.5 µM concentration levels, giving results comparable with those obtained by HPLC/MS/MS analysis.

[1] J.P. Giesy, K. Kannan. Sci. Technol., 35, (2001), 1339.
[2] K. Haupt, K. Mosbach. TIBTECH, 16, (1998), 468.
[3] N. Karimian, A.P.F. Turner, A. Tiwari. Biosens. Bioelectron. 59, (2014), 160.

CLOSING LECTURE

WOLFGANG SCHUHMANN

wolfgang.schuhmann@rub.de

Ruhr-Universität Bochum, Analytical Chemistry – Center for Electrochemical Sciences, Germany

WHAT DO MOLECULES ENCOUNTER AT AN ELECTRIFIED INTERFACE? FROM DNA TO NANOSENSORS

Designing bioelectrochemical interfaces is key for improving highly sensitive analytical devices based either on biochemical recognition processes or biocatalytical conversion of suitable analytes. In this communication, the following aspects are discussed:

1. DNA at an electrified interface.

2. Pulse-potential assisted immobilization of ssDNA and post-modification

3. Reading out DNA hybridization: Electrochemical impedance spectroscopy, surface enhanced Raman scattering, potential pulse assisted dehybridization, enzymatic amplification

4. Controlled fabrication of carbon nanoelectrodes using a newly developed automated device together with identical location TEM measurements

5. Carbon nanoelectrodes as basis for high-sensitive sensors, biosensors and field-effect transistors

POSTERS

ADRIAN BLIDAR

blidar.adrian@umfcluj.ro

Analytical Chemistry Department, "Iuliu Haţieganu" University of Medicine and Pharmacy, Cluj-Napoca

CEPHALEXIN ELECTROCHEMICAL SENSOR BASED ON A MOLECULARLY IMPRINTED POLYMER MODIFIED BORON DOPED DIAMOND ELECTRODE

Adrian Blidar, Bogdan Feier, Cecilia Cristea

Cephalexin (CFX) is a β-lactam antibiotic, part of the cephalosporin group with a broad spectrum, being effective against both Gram positive and Gram negative bacteria. Its effectiveness and broad spectrum lead to the widespread use of this compound, which requires fast and sensitive analytical methods, electrochemical sensors being a good alternative in this case.

Electrochemical techniques even though generally sensitive and suitable for in situ analysis, lack in selectivity. An option to combat this disadvantage is represented by the use of the molecular imprinting technique, which allows the modification of the electrode with a polymeric film which contains cavities complementary in size, shape and chemical functionality with the analyte of interest, acting as biomimetic receptors for the target molecule.

In this direction, we developed a molecular imprinted polymer for the CFX detection, through electropolymerization, which was used to modify a boron doped diamond electrode, an electrode with special characteristics which allowed a large potential window, required for the polymerization procedure. The used method was an indirect one, based on the decrease of the electron transfer process as the CFX molecules were captured in the polymeric film.

Several parameters influencing the performance of the sensor have been optimized and the resulted sensing material yielded good results, proving its selectivity and sensitivity in real samples.

JOANNA ROGIŃSKA

joanna.roginska@univ-lorraine.fr

LCPME, Université de Lorraine, CNRS

A PASSIVE ELECTROCHEMICAL MICROBIAL SYSTEM FOR NITRATE REMOVAL IN FREE SURFACE WATER

Joanna Rogińska, Timothé Philippon, Frédéric Barrière, Christelle Despas, Julien Tournebize, Théodore Bouchez, Alain Bergel, Frédéric Jorand, Mathieu Etienne

The modern agriculture is a great consumer of nitrogen fertilizers which are used in order to reach higher production. It results in many ecological issues such as increased nitrate pollution of rivers and aquifers.

Bioelectrochemical systems have been proposed as an innovative way to depollute various types of wastewater but they have not yet been efficiently applied outside the laboratory. Microbial Fuel Cells are bioelectrochemical systems that exploit the ability of some microorganisms to transfer electrons obtained from oxidation of the organic matter to a solid surface. It is also documented that some bacteria are able to receive electrons directly from a solid to reduce chemical compounds, such as molecular oxygen or nitrate.

The goal of the project is to engineer a simple, passive microbial electrochemical system placed directly in the natural wetlands to enhance the denitrification. This can be achieved by inserting a snorkel electrode vertically into the bottom of wetland, leading to the development of different kinds of biofilms on the electrode in the zones in contact with the sediments or the water. The microbial biofilm located on the part in the sediment will oxidize the organic matter and transfer electrons to the electrode. Those electrons will then flow to the part exposed to the water and used by other bacteria to reduce dioxygen. However, if this reduction is faster than the gas diffusion rate, anoxic zones in the medium are created and in turn nitrate reduction is allowed.

After performing the experiments at a laboratory scale, the system will be applied in the artificial wetland of Rampillon (Seine et Marne, France) built by Irstea to mitigate non-point source pollution from the agricultural field. The aim of this project is to double the current denitrification rate which in Rampillon is around 350 mg $NO^{3-}\cdot m^{-2}\cdot day^{-1}$.

Acknowledgements: Financial support from The French National Research Agency (ANR-17-CE04-0004) is gratefully acknowledged.

JUSTIN WEEKS

justin.weeks@chem.ox.ac.uk

Vincent Group, Department of Chemistry, University of Oxford

ELECTROENZYMATIC NADH RECYCLING FOR SELECTIVE BIOCATALYTIC REDUCTIONS

Justin R. Weeks, Holly A. Reeve, Kylie A. Vincent

Biocatalysts such as oxidoreductase enzymes offer exquisite selectivity under mild reaction conditions, but have proved difficult to exploit in fine chemical electrosynthesis. These enzymes require stoichiometric hydride transfer from the expensive biological NAD(P)H cofactor, which means that their use is only viable when they are coupled with an efficient cofactor recycling method. Glucose or isopropanol in super-stoichiometric quantities are often used to recycle the reduced cofactor, NADH, but this approach suffers from poor atom economy. Electrochemically-driven regeneration of the NADH cofactor is possible but problematic at unfunctionalized electrodes due to formation of non-active forms of the reduced cofactor.

Here, we present an electrochemically-driven NADH regeneration system with NAD+-reductase modified carbon electrodes, offering perfect selectivity for the active NADH cofactor. We show that we can immobilize this enzyme onto carbon interfaces and that it is electrochemically active at much more modest potentials than using unmodified electrodes. We demonstrate this recycling system as a modular approach to biocatalytic reductions, coupling NADH-dependent reductases onto the same carbon interface for efficient hydride transfer. We observe that this electro-biocatalyst is stable over many days of continuous use.

MATS DE JONG

mats.dejong@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

PORTABLE VOLTAMMETRIC SENSOR FOR THE ON-SITE DETECTION OF COCAINE STREET SAMPLES

Mats de Jong, Anca Florea, Joy Eliaerts, Filip Van Durme, Joren Van Loon, Nele Samyn, Karolien De Wael

Consumption, production and distribution of drugs of abuse is an important worldwide issue, resulting into about 310 million illicit drug users worldwide and around 200 000 drug related deaths each year. Cocaine is one of the most prominent drugs, with an average seizure amount of 850 tons each year. Belgium is with the Port of Antwerp and Brussels Airport one of the most important countries of interest in Europe for drug trafficking with around 20 tons of seized cocaine each year.

Customs services at airports and harbours are very keen to monitor passing cargo, luggage and people for the presence of cocaine. The most common on-site screening method is the Scott colour test, based on complexation of cocaine with cobalt thiocyanate, resulting in a blue colour. Despite the ease of use of these tests, they are difficult to interpret and they often give a false result, resulting in confiscation of legal substances (false positive test) or the failure of seizing cocaine (false negative test).

Electrochemistry allows a fast, cheap and sensitive on-site detection of low concentrations of redox active targets. Using graphite screen printed electrodes, strategies were developed for the on-site detection of cocaine with square-wave voltammetry, including the use of different pH and pre-treatment strategies. Extra attention was given to cocaine samples containing levamisole, as this highly abundant cutting agent suppresses the oxidation signal of cocaine. A small portable potentiostat was used for on-site analysis combined with an Android application for the automatic detection of cocaine, useful for customs personnel and police, as a reliable replacement for the colour tests. Over 350 samples were analysed and the specificity and sensitivity of the developed strategy compared to these of the colour test. Also, design concepts for the eventual sensor were considered, tested and evaluated.

VANOUSHE RAHEMI

vanousheh.rahemi@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

ENZYMATIC SENSORS FOR PHENOLS BASED ON REDOX CYCLING WITH PEROXIDASE AND A SURFACE CONFINED SACRIFICIAL ELECTRON ACCEPTOR

Vanoushe Rahemi, Stanislav Trashin, Vera Meynen, Karolien De Wael

Numerous second and third generation biosensors have been elaborated for H_2O_2 sensing based on horseradish peroxidase (HRP). [1] HRP catalyses the oxidation of a wide range of substrates upon adding hydrogen peroxide as a sacrificial electron acceptor. [2] However, the addition of hydrogen peroxide (H_2O_2) typically causes a large drop in background current for electrochemistry-based systems; consequently, additional time is needed to stabilize the background. We found that short pre-treatment by H_2O_2 of electrodes modified by titanium dioxide impregnated by HRP (0.75 nmol per 1 mg of TiO_2) results in accumulation of oxidizing species (ca.14 nmol per 1 mg TiO_2) that cannot be washed in followed multiple washing steps and can serve as an oxidizing agent for HRP. In the presence of 0.5 µM hydroquinone (HQ) the pre-treated electrodes supported a stable cathodic current response (less than 20% decrease) for at least 30 min. Electrodes that were not pre-treated showed no noticeable current response to 0.5 µM HQ. The pre-treated HRP|TiO_2|SPE demonstrated high sensitivity and fast response to hydroquinone, aminophenol, phenol, catechol, caffeic acid, and other phenols. The calibration curve for 4-aminophenol was linear in the range from 0.05 to 1 µM with the sensitivity of 2.7 ± 1.0 $A \cdot M^{-1} cm^{-2}$ (average ±SD of three different electrodes) with the limit of detection of 24 nM. Intriguing, the sensitivity of the pre-treated electrode was 5 times higher than that of the similar electrode in the conventional measurements, i.e. in the presence of 1 mM H_2O_2. The idea of the pre-treatment opens new possibilities for applications of the peroxidase sensors in analysis of phenols in a drop and in flow without H_2O_2 in the measuring solution.

[1] S. Xu, B. Peng, X. Han, Biosensors and Bioelectronics 2007, 22, 1807-1810.
[2] M. Dequaire, B. Limoges, J. Moiroux, J.-M. Savéant, Journal of the American Chemical Society 2002, 124, 240-253.

STANISLAV TRASHIN

stanislav.trashin@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

SINGLET OXYGEN MEDIATED PHOTOCATALYSIS IN BIOANALYTICAL APPLICATIONS

Stanislav Trashin[a], Vanousheh Rahemie[a], Francisco Morales-Yanez[b,c], Saranya T. Shanmugam, Liselotte Neven[a], Katja Polman[b], Serge Muyldermans[c], Sergiu M. Gorun[d], Karolien De Wael[a]

[a]AXES Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium; [b]Department of Biomedical Sciences, Institute of Tropical Medicine, Antwerp, Belgium; [c]Laboratory of Cellular and Molecular Immunology, Vrije Universiteit Brussel, Brussels, Belgium; [d]Department of Chemistry and Biochemistry, Seton Hall University, 07079 New Jersey, USA.

A range of photoreactive compounds (photosensitisers) produce highly reactive singlet oxygen ($^1O_2$) upon light illumination and, thus, they catalyse oxidation of organic molecules that are essentially stable at ambient conditions. The $^1O_2$ mediated photocatalytic oxidation has become an important tool in organic synthesis, environmental chemistry, and photobiology. Surprisingly, little attention had been paid to its application in the field of (bio)analytical chemistry. In our recent publication we reported for the first time on the application of the $^1O_2$ mediated photocatalysis in electrochemical sensors for small organic molecules and affinity recognition [1]. For electrochemical detection of small organic molecules containing phenolic or aminobenzyl- groups, we employed a similar detection scheme as that used in enzymatic biosensors based on oxidases or peroxidases. Literally, an analyte undergoes the redox cycling between an electrode and a photocatalyst. As a rational choice we used, we used a fully fluorinated Zn phthalocyanine complex – an efficient yet stable photosensitizer producing $^1O_2$ [2]. For affinity sensors, two detection schemes can be implemented. The first scheme suggests amperometric detection of $^1O_2$ generated by a molecular photosensitizer attached to a detection biomolecule, while in the second scheme, the oxidation of an added redox reporter was detected. The usefulness of the photocatalysis was shown for both DNA and immunosensors. Singlet oxygen mediated photocatalysis can be a powerful and versatile tool in electroanalysis giving new opportunities for creating more robust and stable electrochemical sensors functioning in conditions when biosensors, e.g. HRP-based sensors, may fail due to vulnerability of biocatalysts to temperature, pH, and organic solvents.

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

[2] R. Gerdes, L. Lapok, O. Tsaryova, D. Wohrle, S.M. Gorun. Rational design of a reactive yet stable organic-based photocatalyst. Dalton Trans., 2009, 1098-1100.

ANCA FLOREA

anca.florea@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

BIOMIMETIC PLATFORMS FOR SELECTIVE ELECTROCHEMICAL DETECTION OF COCAINE

Anca Florea[a], Todd Cowen[b], Sergey Piletsky[b], Karolien De Wael[a]

[a] *AXES Research Group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171 - 2020 Antwerpen – Belgium.*
[b] *University of Leicester, Department of Chemistry, LE1 7RH, UK*

Electrochemical methods have gained increasing interest for the detection of illicit drugs, due to their rapidity, simplicity and low cost. The development of sensing systems based on the combination of molecular imprinted polymers (MIP) with electrochemical transduction represents a promising approach for sensitive and selective detection of drugs in complex matrices. Among the preparation methods for MIP, electropolymerization is a simple and convenient way, allowing to easily control film thickness and obtain thin, adherent films in one-step, directly on the surface of the transducer.

We present the development of the first amperometric sensor based on MIP for direct detection of cocaine in street samples. Monomers with high recognition ability for cocaine were selected by computational modelling and deposited directly on the surface of graphene-modified electrodes via electropolymerization. Firstly, poly(p-aminobenzoic acid) and poly(o-phenylenediamine) layers were employed in voltammetry studies and compared in terms of binding affinity and electrochemical response towards cocaine; p-aminobenzoic acid was further selected as monomer for MIP synthesis.

The integration of nanoparticles in MIP materials has the benefit of enhancing the number of accessible complementary cavities, the catalytic activity of the surface and the fast equilibration with the analyte.

FABIO BOTTARI

fabio.bottari@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

GRAPHITE SCREEN PRINTED ELECTRODE DECORATED WITH ELECTROPOLYMERIZED O-PHENYLENDIAMINE FOR THE DIRECT ELECTROCHEMICAL DETECTION OF NAFCILLIN

F. Bottari[a], G. Moro[a], A. Florea[a], S. Piletsky[b] and K. De Wael[a]

[a] *AXES Research Group, Department of Chemistry, University of Antwerp, Groenenborgerlaan 171 - 2020 Antwerpen – Belgium.*
[b] *University of Leicester, Department of Chemistry, LE1 7RH, UK*

The analytical determination of residues of β-Lactam antibiotics in the environment is a fundamental issue for authorities and consumers. For these reasons, novel analytical screening tools are needed to perform continuous and on-site monitoring of these contaminants. In this scenario, electrochemical sensors could be the answer, coupling the sensibility of electrochemical methods with the user-friendliness and low cost of equipment, and easy data handling. Here is presented a polymer-modified graphite electrode for the direct electrochemical determination of nafcillin, an antibiotic that belongs to the family of penicillins, which is difficult to detect with traditional screening test [1-2]. The graphite screen printed electrode (G-SPE) was decorated with electropolymerized orto-phenylediamine (OPD) to promote the interaction of the antibiotic with the electrode surface. OPD was selected by rational monomer design. All the experimental parameters were optimized, namely monomer concentration, pH, number of electropolymerization cycles to obtain the highest signal for the target, and the electrode was characterized with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The identification of nafcillin is based on the oxidation peak at +1.1 V (vs pseudo Ag) that is due to the antibiotic's side chain. With the optimized modification protocol, a three-fold increase in nafcillin signal was obtained: the calibration plot in 0.1 M Britton-Robinson buffer pH4 showed a LOD of 80 nM with a good sensitivity and reproducibility (STD>5%). The prototype sensors is ready to be applied in different real matrices like milk, waste water and other environmentally relevant samples.

[1] Reybroeck, W. and Ooghe, S., Journal of AOAC International, 2011, 94 (2), 373-382.
[2] Reybroeck, W., et al., Food additives & contaminants. Part A, Chemistry, analysis, control, exposure & risk assessment, 2010, 27 (8), 1084-1095.

FRANCISCO MORALES

Francisco.Morales.Yanez@vub.be

Laboratory of Cellular and Molecular Immunology, Vrije Universiteit Brussel, Department of Biomedical Sciences, Institute of Tropical Medicine, Antwerp

ULTRASENSITIVE DETECTION OF TOXOCARA CANIS EXCRETORY-SECRETORY ANTIGEN BY A NANOBODY ELECTROCHEMICAL MAGNETOSENSOR ASSAY

Francisco Morales-Yanez[a,b], Stanislav Trashin[c], Marie Hermy[b], Idalia Sariego[d], Karolien De Wael[c], Katja Polman[b], Serge Muyldermans[a]

[a]Laboratory of Cellular and Molecular Immunology, Vrije Universiteit Brussel, Brussels, Belgium; [b]Department of Biomedical Sciences, Institute of Tropical Medicine, Antwerp, Belgium; [c]AXES Research Group, Department of Chemistry, University of Antwerp, Antwerp, Belgium, [d]Department of Parasitology, Institute of Tropical Medicine Pedro Kourí, Havana, Cuba.

Human Toxocariasis (HT) is a zoonotic disease caused by the migration of the larval stage of the roundworm *Toxocara canis* in the human host. Despite of being the most cosmopolitan helminthiasis worldwide, its diagnosis is elusive. Currently, the detection of specific immunoglobulins IgG against the Toxocara Excretory-Secretory antigen (TES), combined to clinical and epidemiological criteria is the only strategy to diagnose HT. Cross-reactivity with other parasites and the inability to distinguish between past and active infections are the main limitations of this approach. Here, we present a sensitive and specific novel strategy to detect and quantify TES, aiming the identification of active cases of HT. High specificity is achieved by making use of nanobodies (Nbs), single domain antibodies obtained from camelids, which due to their small molecular size (15kDa) can recognize hidden epitopes not accessible to conventional antibodies. High sensitivity is attained by the design of an electrochemical magnetosensor with an amperometric read-out with all components of the assay mixed in one single step. Through this strategy, 10-fold higher sensitivity than a conventional sandwich ELISA was achieved. The assay reached a limit of detection of 2 and15 pg/ml in PBST20 0.05% and serum spiked with TES, respectively. These limits of detection are sufficient to detect clinically relevant toxocaral infections. Furthermore, our nanobodies showed no cross-reactivity with antigens from *Ascaris lumbricoides* or *Ascaris suum*. This is to our knowledge, the most sensitive method to detect and quantify TES so far, and has great potential to significantly improve diagnosis of HT. Moreover, the characteristics of our electrochemical assay are promising for developing point of care diagnostic systems using nanobodies as a versatile and innovative alternative to antibodies. The next step will the validation of the assay in a clinical and epidemiological context.

NICK SLEEGERS

nick.sleegers@uantwerpen.be

AXES Research group, Department of Chemistry, University of Antwerp

THE ELECTROCHEMICAL FINGERPRINT OF INTACT CEPHALOSPORIN ANTIBIOTICS: THE GROUNDWORK FOR A SMART VOLTAMMETRIC MONITORING STRATEGY

Nick Sleegers[a], Alexander van Nuijs[b], Karolien De Wael[a]

[a]*University of Antwerp, AXES Research Group, Groenenborgerlaan 171, B-2010, Antwerp, Belgium*
[b]*University of Antwerp, Toxicological Centre, Universiteitsplein 1, 2610, Wilrijk, Belgium*