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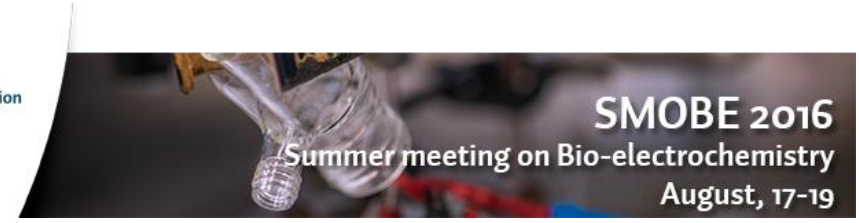

Room K2.01

Kleine kauwenberg 14-22

B-2000 Antwerpen

ABSTRACTS

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TUTORIAL LECTURES

ELISABETH LOJOU

lojou@imm.cnrs.fr

French National Centre for Scientific Research, France

ENZYME ELECTRICAL CONNECTION IN BIOFUEL CELLS

Fuel cells are envisioned to take up the energy challenges launched by fossil fuel exhaustion. One of their drawbacks relies on the need of chemical catalysts mainly based on platinum to accelerate the electrode reactions. Biology offers an attractive alternative thanks to the use of biodegradable, efficient and specific enzymes as biocatalysts in biofuel cells. However, this biofuel cell development requires as a first step that the biocatalysts are efficiently connected to the electrodes. Simply considering the size of the biological object, the fact that the active site is buried inside the isolating protein moiety, strategies must be engaged to succeed in the electrical connection of the enzymes.

In this course we will first 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 the key issue is the orientation of the biological object. We will present some chemical modifications of the electrodes that can control the biocatalyst orientation, then the electron transfer rate, and finally the catalysis.

Secondly, 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. 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.

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DIRK HEERING

dirk.heering@wur.nl

Wageningen University, Physical Chemistry and Soft Matter, the Netherlands

ELECTRO-ENZYMOLOGY: ELECTROCHEMISTRY OF WIRED REDOX ENZYMES

Electro-enzymological experiments can be regarded a multi-dimensional high-throughput version of the classical cuvette activity assay. Interfacial electron transfer and mass transport are coupled to inter- and intra-protein electron transfer, and chemical processes such as proton transfer and conversion of substrate to product in the active site. With the help of direct data analysis, and mathematical modeling and simulations, a wealth of biochemically relevant information can be derived from multi-dimensional turnover rate traces.

To study redox enzymes with electrochemical methods, optimization of experimental parameters such as solution composition, current/voltage/time settings and methods, mass transport and cell geometry is pivotal. A particularly critical point is the interaction between enzyme and electrode. The interaction needs to be both intimate and vectorial to achieve fast and site-specific interfacial electron transfer. However, direct interaction between the protein and the (metallic) electrode surface is often detrimental. Modification of the surface with e.g., alkane thiols may render it bio-compatible and site-specific, but this usually severely impedes electron transfer.

These conflicting requirements can all be met by using a natural substrate as electrode-modifier. This can be a small, robust redox protein such as cytochrome c that rapidly exchanges electrons with both the electrode and the enzyme such as cytochrome c oxidase (respiratory complex IV). Another strategy is designing a specific “molecular wire”, i.e., a conjugated molecule with substrate functionality. We have designed and synthesized novel, bifunctional oligo(phenylenevinylene) (OPV) molecular wires of different length, equipped with a gold binding methyl thiol anchor group on one side and either a bio-identical ubiquinone or menaquinone head group on the other. The wires are designed such that the quinone group retains its natural redox and proton-binding properties, as well as the ability to orient to and bind in the active site of enzymes that use a specific quinone as natural substrate. SAMs of these wires provide a well-defined electron pathway between the gold electrode and the enzyme. This opens the way to study complex Q-dependent respiratory enzymes.

THOMAS DONEUX

tdoneux@ulb.ac.be

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

ELECTROCHEMISTRY AND NUCLEIC ACIDS: A BRIEF TUTORIAL

Electrochemistry is a wonderful tool for studying nucleic acids. Nucleic acids are indeed electroactive since the nucleic bases can be reduced or oxidized at various electrodes. Nucleic acids are also polyelectrolytes and are thus sensitive to the charge and electric field distributions -key quantities for electrochemists-. Moreover, nucleic acids display a broad range of interactions (covalent, intercalation, groove binding...) with synthetic or natural ligands, many of them being also electroactive.

In the realm of popular imagination, DNA is unambiguously identified with the famous Watson-Crick double-helix structure, also known as "B-DNA". Yet, it is nowadays well-established that nucleic acids are much more diverse than just double-helices, and many other structures, such as A-DNA, Z-DNA, triplexes, G-quadraplexes, i-motifs, hairpins, three-way junction,... have been identified. These non-canonical structures markedly expand the field of nucleic acid electrochemistry, offering new scientific challenges and opportunities to bioelectrochemists.

After providing a non-exhaustive overview of the above-mentioned topics involving electrochemistry and nucleic acids, this communication will focus on some selected work from the author's laboratory. These examples are aimed at showing the powerful potentialities of electrochemical DNA-based biosensing, at underlying the importance of biosensors interfacial architecture, and at illustrating an electrochemical investigation of G-quadruplex – ligands interactions.

PRESENTATIONS

LO GORTON

Lo.Gorton@biochemistry.lu.se

Lund University, Biochemistry, Sweden

DIRECT ELECTRON TRANSFER BETWEEN CELLOBIOSE DEHYDROGENASE AND ELECTRODES AS BASIS FOR 3RD GENERATION BIOSENSORS/BIOANODES

Lo Gorton, Christopher Schulz, Roland Ludwig

Cellobiose dehydrogenase (CDH) is an extracellular monomeric two domain redox enzyme composed of an FAD containing dehydrogenase domain (DHCDH) connected with a heme b containing cytochrome domain (CYTCDH) through a flexible linker region. CDH is produced by Basidiomycota (class I) and Ascomycota (class II) and is involved in the degradation of cellulose, where it oxidizes products of cellulose: i.e., cellodextrins formed from cellulose by cellulases. Lactose is also oxidized and some CDHs may oxidize glucose. The oxidation of the substrate by CDH leads to the full reduction of the FAD cofactor to FADH2. In nature the final electron acceptors were found to be copper dependent, lytic polysaccharide monooxygenases, which are suggested to react with molecular oxygen to form reactive oxygen radicals assisting in the decomposition of the lignocellulose matrix [1].

Both class I and II CDHs are since a long time known for their efficient direct electron transfer (DET) characteristics with electrodes [2,3], which in turn have resulted in making 3rd generation biosensors for both lactose and glucose. However, until recently it was believed that DET was possible only through the CYTCDH acting as a built in redox mediator. In contrast we have now shown that under certain conditions very efficient DET reactions can be obtained directly between the DHCDH and electrodes at least for class I CDHs [4]. An efficient DET between the DHCDH should largely facilitate the use of CDH modified electrodes in both biosensors and bioanodes.

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ILARIA PALCHETTI

ilaria.palchetti@unifi.it

University of Florence, Department of Chemistry "Ugo Schiff", Italy

ELECTROCHEMICAL BIOSENSING PLATFORMS FOR MIRNA DETECTION

Since their discovery in 1993 in the soil nematode Caenorhabditis elegans by the Ambros group, over the last decades miRNAs (microRNAs, miRs), a large class of small noncoding RNAs with approximately 20 nucleotides in length, have been considered to play important roles in different biological processes such as cell differentiation, proliferation and regulation of protein translation. An abnormal miRNA expression (over-expression or down-expression) has been correlated with cancer and other diseases. Tumor-derived miRNAs are present in human body fluids such as serum, plasma, urine, saliva and sputum. As a result of their tissue specificity and relative stability, circulating miRNAs offer great potential for use as minimally invasive diagnostic, prognostic and predictive tumor biomarkers. Currently, different analytical methods can be used to detect miRNAs (i.e. microarrays, quantitative Real-Time PCR (qRT-PCR) and next-generation sequencing); each of these methods is characterized by their own unique advantages and disadvantages. Among them, qRT-PCR is commonly used due to the inherent sensitivity and reliability. However, the small size of miRNAs greatly complicates the use of PCR based methods. Electrochemical genosensors have emerged as particularly attractive PCR-free options owing to their appropriate sensitivity, multiplexing capability, and their simplicity to use and the small amount of sample required.

Electrochemical techniques, such as faradic impedance spectroscopy, chronoamperometry, and differential pulse voltammetry, have been used by our group, for the development and characterization of biosensors for miRNAs detection. Basically, DNA capture probes have been immobilized on the electrode surfaces. Total RNA has been extracted from the sample, biotinylated, and then hybridized with the specific capture probes. Then, the biosensing platform has been incubated with streptavidin alkaline phosphatase and exposed to a proper substrate. The product of the enzymatic reaction has been electrochemically monitored. Biotin labeled liposomes have been also tested as a functional tether for the enzyme molecules. Dendritic-type amplification of a target miRNA has been also accomplished by the use of streptavidin and biotinylated alkaline phosphatase, which can be self-assembled to build nanoarchitectures rich in enzyme label.

In a further approach, a label-free impedimetric genosensor has been developed, using a miniaturized, polymer-modified sensor. In particular, a polymer bearing an intact biotin moiety available for streptavidin binding has been used. As a result, the sensor surface has been nanostructured, thus increasing the capture probe immobilization efficiency in terms of orientation, loading and steric hindrance.

PATRICK WAGNER

patrickhermann.wagner@kuleuven.be

KULeuven, Soft-Matter Physics and Biophysics Section ZMB, Belgium

BIODETECTION IN 'REAL' SAMPLES USING IMPEDANCE SPECTROSCOPY AND THERMAL BOUNDARY EFFECTS

In this contribution, I will give an overview on some recent developments in label-free biosensing: Impedance spectroscopy is already well established and examples include i) the detection of SNP mutations in DNA by real-time denaturation monitoring, (ii) the detection of serotonin in human blood plasma, and iii) the detection of histamine in bowel liquids. Key ingredients are a differential sensing technique to compensate for non-specific adsorption effects and the use of molecularly imprinted polymers (MIPs), being extremely stable, synthetic receptors. The sensing effect in these three examples is based on an alteration of the capacitance at the solid-liquid interface upon molecular recognition. Interestingly, changes at the solid-liquid interface also have a measurable impact on the thermal resistance of this interface: The technique requires not more than a heat source to create a temperature gradient across the interface and two temperature sensors, one underneath the chip and one above the chip in the liquid. This technique, called the 'heat-transfer method HTM', was successfully applied for mutation analysis, for the detection of small signaling molecules, for protein- and cell detection, and for monitoring structural phase transitions in lipid vesicles. The detection limits obtained with HTM come close to the sensitivity of impedance spectroscopy while HTM can also operate in combination with non-conducting liquids and with electrically isolating sensor-chip materials. Until date, there is little understanding on the physical origin of these thermal-boundary effects; however, there is evidence that the mismatch of vibrational frequencies between the chip (phonons), the bio-layer, and the liquid might play a role.

MATS DE JONG

Mats.dejong@uantwerpen.be

Universiteit Antwerpen, AXES, Belgium

PORTABLE VOLTAMMETRIC SENSOR FOR FAST, SENSITIVE AND SELECTIVE ON-SITE SCREENING OF COCAINE

Mats de Jong, Nick Sleegers, Jayoung Kim, Filip Van Durme, Nele Samyn, Joseph Wang, Karolien De Wael

Consumption, production and distribution of drugs of abuse is an important worldwide issue, resulting into about 250 million illicit drug users worldwide and around 200 000 drug related deaths each year. Cocaine is one of the most prominent compounds, as well as one of the most addictive and dangerous ones, with an average seizure amount of 700 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 dealers with around 20 tons of seized cocaine each year.

Customs services at airports and harbors are very keen to monitor passing cargo, luggage and people for the presence of cocaine. The most common on-site screening method these days is the Scott color test, based on complexation of cocaine with cobaltthiocyanate, resulting in a blue color. Despite the ease of use and good sensitivity of these tests, in about 5 % of cases, the test gives a false result, resulting in confiscation of legal substances (false positive test) or the failure of seizing cocaine (false negative test). Selectivity is thus a major problem.

Electrochemistry allows a fast, cheap and sensitive on-site detection of low concentrations of redox active targets. Altering reaction conditions and adding aptamers as bio-recognition elements will deliver improved selectivity, resulting into a both sensitive and selective mobile electrochemical aptasensor for cocaine.

Results will be presented concerning the development of a screening method for on-site cocaine detection. The following aspects will be addressed: (1) assembling the voltammetric fingerprint of typical cocaine (street) samples; (2) voltammetry of substances causing false positive and negative results with the color tests; (3) immobilization of aptamers on graphite screen-printed electrodes using polysilane films and the effect on the voltammetric signal for cocaine.

SÉBASTIEN DELILE

sebastien.delile@univ-paris-diderot.fr

Université Paris Diderot, UMR CNRS, France

HIGH THROUGHPUT SCREENING OF THE AFFINITY AND THERMODYNAMIC OF REDOX MOLECULES BINDING ON DS-DNA WITH A TEMPERATURE MODULATION

Sébastien Delile, Ashwani Sharma, Claire Fave, Aurélie Perrier, Damien Marchal

To detect and quantify DNA quantities as small as one molecule in biological samples by working faster, cheaper and with a better accuracy, is still a challenging research field with applications in molecular diagnostics as well as in food safety or environmental survey. The currently most used techniques are in-vitro DNA amplification procedures such as polymerase chain reaction (PCR) coupled with fluorescence detection. In spite of effectiveness, the fluorescence spectroscopy suffers from major drawbacks like the chemical stability of the probes and the high cost of the instrumentation, which can all be overpassed by using electrochemistry as amplified DNA detection method [1].

The electrochemical real-time detection principle is based on the redox current decrease of a redox DNA-bound probe as compared to the freely diffusing initial one. Accordingly, ideal probe should have an easily measurable redox couple, a relatively high affinity (Kb > $10^{\wedge 5}$ L/mol) with double-stranded DNA even at the working temperature (i.e. 60 to 75°C) and shouldn't inhibit the amplification process [1].

A custom-designed [2] thermocycler including a 48-well electrochemical microplate and a multiplexed potentiostat was used to easily screen the binding affinity of numerous probes. By this way, it wis possible to determine the binding constant and all the thermodynamic parameters of a probe with ds-DNA within a single experiment. These data were used to explain the previously found efficiency of phenazine complexes of osmium, methylene blue and its derivatives for different in-vitro DNA amplifications. [1,3]

Finally, combining a molecular modeling study and this experimental method allows us to select, synthetize and evaluate a new class of redox probes aiming at enhancing the DNA amplification monitoring of PCR.

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LIGIA MARIA MORETTO

moretto@unive.it

University Ca' Foscari of Venice, Laboratory of Electrochemical Sensors, Department of Molecular Sciences and Nanosystems, Italy

DETECTION OF DIFFERENT ISOTYPES OF ANTI-TISSUE TRANSGLUTAMINASE BY NANOELECTRODE ENSEMBLE BIOSENSORS FOR CELIAC DISEASE DIAGNOSTICS

Ligia M. Moretto, Paolo Ugo, Henok H. Baye, Sara Longo

Celiac disease (CD) is a gluten-induced autoimmune disorder with prevalence of about 1% of the population. To reduce the morbidity and the mortality associated to CD, simple and effective methods to perform screening tests for early diagnosis and follow-up tests for patients on gluten-free diet are necessary. Many recent research efforts are aimed at developing tests to detect anti-tTG in serum samples, since its level decreases when the celiac patient assume gluten.

Anti-tTG immunoglobulins are classified into two isotypes, IgA and IgG. Immunoglobulin A (IgA anti-tTG) is the isotype typically determined as target analyte for serological CD screening. However, IgA-deficient CD patients and patients younger than 2 years of age are not identified by this analysis. To overcome these limits, we present a novel electrochemical immunosensor based on nanoelectrode ensembles (NEEs) able to detect, with suitable sensitivity and selectivity, both the IgG and IgA isotypes of anti-tTG. NEEs are prepared by template electroless deposition of gold in track-etched polycarbonate membranes (PC). The PC surface of NEEs is functionalized with tissue transglutaminase (tTG) as the capture antigen able to bind both the isotypes IgA and IgG of anti-tTG from serum samples. The selective detection of the isotypes is possible using two differently labelled secondary antibodies: anti-IgG sec-Ab labelled with horseradish peroxidase (HRP) and anti-IgA sec-Ab labelled with glucose oxidase (GOx). The addition of the suitable substrate (hydrogen peroxide or glucose) in the presence of an appropriate mediator (hydroquinone or (ferrocenyl-methyl)trimethylammonium)) gives signals that scale with the concentration of the relevant immunoglobulin isotype. The analytical performances of the NEE-based immunosensor are evaluated by determining both IgA and IgG anti-tTG in human serum samples.

VALENTINA GRIPPO

v.grippo@chem.uw.edu.pl

Warsaw University, Renata Bilewicz Group, Poland

LIPIDIC CUBIC PHASE FOR HOSTING ENZYMES AND IMPROVING THEIR CATALYTIC ACTIVITY

Valentina Grippo, Roland Ludwig, Renata Bilewicz

Lipid cubic phase systems are an excellent immobilizing carriers for enzymes due to their biocompatibility and well-defined pore nanostructure.1 They have been proposed as a convenient matrix for incorporating enzymes and holding them on the electrode surface in a fully active form. Biofuel cells based on cubic phase do not need additional separating membranes and can be easily miniaturized. The lipidic membrane is stable in the presence of water. 2

We used cubic phase for immobilizing Corynascus thermophius CDH (CtCDH). CDH is an extracellular oxidoreductase secreted by wood degrading fungi. It oxides sugars to their respectively lactones. The two electrons gained during the process are transferred to a monooxygenase which reacts with oxygen to form radicals and carry out the wood decomposition. It consists of two separates domains joined together with a short polypeptide linker region. The larger domain is the flavodehydrogenase domain (DHCDH), and it is the catalytically active. Electrons can be transferred to a one or two-electrons acceptor (in mediated electron transfer conditions, MET) or alternatively can be shuttle through an internal electron transfer (IET) to the cytochrome domain (CYTCDH). Electrons are then transferred in direct electron transfer (DET) conditions to the natural acceptor or to the electrode surface.

Here we report the improvement gained by the CtCDH when trapped in a monoolein cubic phase in mediated and direct electron transfer conditions. Ruthenium ammonium chloride, $Ru(NH_3)Cl_2$, midpoint potential at pH 7.4 equal to -136 mV, was successfully used ad mediator.

KAREN LEVRIE

karen.levrie@imec.be

imec / KU Leuven, Life Science Technologies, Belgium

MULTIPLEXED SITE-SPECIFIC ELECTRODE FUNCTIONALIZATION BY COMBINING ELECTROGRAFTING AND CLICK CHEMISTRY

Karen Levrie, Karolien Jans, Niyousha Ardakanian, Niels Verellen, Chris Van Hoof, Liesbet Lagae, Tim Stakenborg

Multitarget biosensors hold great promise to improve numerous fields such as genomics, proteomics, drug discovery, medical diagnosis and therapy monitoring. The simultaneous detection of different biomolecular markers, like genes, proteins, or a combination of both, helps pave the way towards advanced point-of-care diagnostics. The functionalization of these multitarget biosensors, however, necessitates patterned immobilization of different bioreceptors, which remains challenging and time consuming. We present a fast and straightforward method for the patterned multiplexing of bioreceptors on a multi-electrode array. Using the electrodes not only for readout, but also for surface functionalization, overcomes the need for additional patterning steps. The proposed method for self-aligned immobilization offers a spatial resolution that is solely limited by the lithographic electrode patterning process and that cannot be easily obtained by alternative dispensing or coating techniques. Moreover, a wide range of electrode materials can be used for the same procedure.

Via electrochemical reduction of aryl diazonium salts in combination with 1,3 cycloaddition click chemistry, we achieved site-specific immobilization of two different ssDNA probes side by side on a single chip. This method was experimentally verified by cyclic voltammetry, X-ray photoelectron spectroscopy and grazing angle Fourier transform infrared spectroscopy, and specific target recognition was visualized by confocal fluorescence microscopy. By combining the electroaddressability of electrografting with the chemoselectivity of click chemistry, we demonstrate a versatile platform for the rapid and highly efficient site-specific functionalization of multitarget biosensors.

LIZA RASSAEI

L.Rassaei@tudelft.nl

Delft University of Technology, Laboratory of Organic Materials and Interfaces, the Netherlands

NANOGAP SENSORS

In the view of growing interest in bioanalytical devices, in this talk, I address current challenges in all-electrical biosensing systems as these systems scales down towards the nano/microdimension with a main focus on electrochemical nanofluidic devices as an example.

Electrochemical nanofluidic channels incorporating two planar microelectrodes (~ 10-50 µm) separated by a thin layer of fluid (with a thickness of <100 nm) are fabricated on a chip. The fabrication is carried out by photolithographic patterning in a way that the nanofluidic device is encapsulated in silicon dioxide with two access holes. Access holes allow the etching solution to reach and remove the sacrificial layer, leaving behind a nanoscale cavity. Redox active molecules can freely diffuse in and out of the channel and undergo electrochemical redox cycling at both suitably-biased potentials. As these molecules are able to repetitively undergoing oxidation and reduction, each molecule can transfer, on average, thousands of electrons by repeatedly traveling between the electrodes before escaping back out into the bulk resulting in a boost in sensitivity and selectivity. In a recent work, we developed a bionanofluidic sensor where we combined an enzymatic recognition element (tyrosinase) and electrochemical signal transduction within a six-femtoliter volume. Tyrosinase catalyzes the oxidation of redox inactive monophenols into redox active diphenols and quinones in the nanochannel. We show how this can lead to a novel bionanofluidic sensor for sensitive detection of minute amounts of phenolic compounds and how to tune selectivity in such sensors.

CECILIA CRISTEA

ccristea@umfcluj.ro

Iuliu Haţieganu University of Medicine and Pharmacy, Analytical Chemistry Department, Romania

ELECTROCHEMICAL ASSAYS FOR CANCER DIAGNOSIS AND PROGNOSIS

Cecilia Cristea, Anca Florea, Mihaela Tertis, Oana Hosu, Bianca Ciui, Robert Sandulescu

The third millennium encounters a very demanding challenge: there are more and more cancer patients, as a direct consequence of continuous increase of the world population, higher average life span and treatment for competing co-morbidities. This makes cancer one of the main causes of deaths nowadays, due to a complex set of uncontrollable natural and artificial factors. Advances in cancer management depend on early cancer diagnosis, prevention of recurrence and drug selection based on genetic profiling and personalized treatment. Nanomaterials can have a great impact on each of these levels. Early stage cancer diagnosis is desirable to prevent metastasis, but remains challenging because clinical symptoms usually appear only in advanced stages of cancer. An important step is to perform this early stage detection by using none or minimal invasive techniques, requiring a fast and accurate response. Natural or synthetic materials could be used, such as antibodies, aptamers, polymers, carbon based nanomaterials (nanotubes, graphene, fullerene), superparamagnetic iron oxide, and their composites in the design and optimization of sensitive and specific sensors.

Cancer biomarkers, like any other biomarker, are generally defined as “a characteristic that is objectively measured and evaluated as an indicator of normal biological processes, pathogenic processes, or pharmacological responses to a therapeutic intervention”. Their abnormal levels appear from early stages of cancer; therefore they could be used in early detection improving the survival rate of patients. Cancer biomarkers are currently detected by using immunoassays; the design of novel electrochemical assays being of interest for our group. Electrochemical immunoassays for early diagnosis of cancer are a promising field, with future helpful perspectives in clinical diagnosis. The limiting factor of their commercialization relies on the lack of internal validation, the long term stability and the length and (sometimes) complicated protocols used for immuno/aptasensors incorporating nanomaterials.

Examples of electrochemical assays using different types of nanomaterials for cancer biomarkers and antineoplastic drug detection will be discussed.

KASPER EERSELS

kasper.eersels@fys.kuleuven.be

KULeuven, Soft-Matter Physics and Biophysics Section ZMB, Belgium

THERMAL BIOSENSORS FOR CELL DETECTION

This contribution aims at providing an overview of the applicability of a recently developed thermal sensing concept for cell identification. The key element of the platform consists of a surface-imprinted polymer (SIP) layer, a robust and stable synthetic cell receptor that is able to rebind cells in a very selective manner. Whenever, a cell, present in the analyte under study, binds to the receptor, the thermal resistance at the solid-liquid interface changes. These changes can be measured by the so-called “heat-transfer method or HTM”. This thermal sensing technique only requires a heat source, to create a temperature gradient across the thermal interface, and two thermocouples to monitor the temperature underneath and above the chip respectively. The platform has successfully been used for the detection of macrophages, cancer cells and bacteria in buffer. Although the sensor is very selective, the sensitivity needs to be improved when aiming at cell identification in biological or environmental samples (whole blood, blood plasma or – serum, drinking water…). Therefore, we have developed a new flow cell for HTM measurements that focuses the heat flow through the sample, leading to a more stable signal. In addition, the sensor platform was used as an assay for monitoring the quality of cell cultures, an application that does not require a high degree of sensitivity.

ANCA FLOREA

florea.ancas@yahoo.com

Iuliu Haţieganu University of Medicine and Pharmacy, Analytical Chemistry Department, Romania

MOLECULAR IMPRINTED ELECTROCHEMICAL SENSORS FOR BIOMEDICAL AND ENVIRONMENTAL ANALYSIS

Anca Florea, Cecilia Cristea, Nicole Jaffrezic-Renault, Robert Sandulescu

Molecular imprinting is a versatile technique for the fabrication of biomimetic receptors, with a wide range of applications in chromatographic separation, solid phase extraction, membrane separation and chemosensors. The imprinting process produces synthetic polymers with cavities complementary in size, shape and chemical functionality with the analyte of interest, which are able to recognize and bind the analyte from complex matrices with high selectivity. MIPs have the advantages over their biological counterparts of ease of synthesis, low cost, high thermal and chemical stability and long storage life.

The integration of MIPs in chemical sensors has received a special attention lately. MIP based electrochemical sensors have been applied with promising results in various fields, such as clinical, bioanalytical and environmental analysis.

Several studies have been proposed for the development of electrochemical MIP-sensors for the sensitive and selective detection of various target analytes, such as drugs and pollutants. TNT, gemcitabine, tetracycline, estradiol and glyphosate have been investigated as template molecules. A generic protocol for the fabrication of MIP was developed based on electropolymerization of p-aminothiophenol functionalized-gold nanoparticles. In order to obtain imprinted films, the electropolymerization process was performed in the presence of the target analyte which serves as template molecule, the subsequent removal of the template leaving cavities that serve as specific recognition sites. Combining the advantages of molecular imprinting and electrodeposition with those conferred by gold nanoparticles, the developed sensors exhibited good sensitivity and high selectivity. Several parameters influencing the performance of the sensors have been optimized and the resulted sensing materials have been successfully applied for the analysis of real samples.

VANOUSHEH RAHEMI

Vanousheh.rahemi@uantwerpen.be

University of Antwerp, AXES, Belgium

IMPREGNATED COMMERCIAL MESOPOROUS TITANIUM DIOXIDE WITH HORSERADISH PEROXIDASE FOR BIO-ELECTROCHEMICAL APPLICATIONS

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

Porous materials are finding important applications in the fields of science and technology as adsorbents, supports for catalysis and (bio)sensors. Because of their large surface and uniform pore size distribution in the same dimensions as biomolecules [1], mesoporous materials have been immobilized on electrodes and impregnated with biomolecules to form biosensors. Recently, it has been proven that the electrode modified with porous TiO_2 (pore size 5-10 nm) and an enzyme can show enhanced catalytic performances [2].

An adhesive conducting electrode material consisting of a biocompatible ion exchange polymer nafion® and commercial mesoporous TiO_2 impregnated with horseradish peroxidase (HRP) is prepared and characterized by amperometric, UV-Vis and N_2 sorption methods. The factors influencing the performance of the resulting biosensor are studied in detail. The optimum conditions for the detection of hydroquinone are an applied potential of -0.1 V and 1 mM hydrogen peroxide. The N_2 sorption results show that the pore volume of TiO_2 decreases sharply upon adsorption of HRP. The preparation process of the proposed enzyme electrode is straightforward and can be potentially used for the preparation of carbon paste electrodes for bioelectrochemical detections.

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ANNA ESPINOZA

anna.espinozat@alumnos.usm.cl

Universidad Técnica Federico Santa María, LMMBA, Chile

TOLUENE DEGRADATION IN BIOELECTROCHEMICAL SYSTEMS USING A PURE CULTURE OF CUPRIAVIDUS METALLIDURANS CH34

Espinoza, A. Franzetti, M. Daghio, M. Seeger

Bioelectrochemical systems (BESs) have proven to be a useful tool for bioremediation and have been applied to achieve the oxidation of organic compounds (e.g. hydrocarbons) at the anode. Microbial metabolism can be stimulated in a BES when overpotential is applied, increasing the rate of pollutant degradation. The aim of this work was to test the exoelectrogenic capacity of Cupriavidus metallidurans CH34 and to determine if the application of overpotential stimulates microbial metabolism to bioremediate toluene-polluted water.

Exoelectrogenic activity was studied with succinate as sole carbon source. Cupriavidus metallidurans CH34 showed exoelectrogenic activity (maximum current density obtained was 0.65 mA/m2), reaching a 91.74% of succinate removal in 42 h.

Although whole genome sequencing reveal that C. metallidurans CH34 lacks in the upper pathway of toluene degradation in anaerobic conditions, C. metallidurans CH34 significantly reduced the concentration of toluene under denitrifying conditions. A Microbial Fuel Cell (MFC) and a Microbial Electrolysis Cell (MEC) were set with a pure culture of C. metallidurans CH34 and with toluene as sole carbon source. In the MEC, overpotential (+800 mV) was applied between the anode and the cathode.

When C. metallidurans CH34 was inoculated in a MFC containing toluene as sole carbon source, current densities reached 0.80 mA/m2, and toluene decreased by 36.6% in 10 days.

In the biotic MEC, current densities increased from 21 to 30 mA/m2 in 20 days, while in the control, current densities remained constant. After the initial adsorption of toluene on the anodes of both inoculated and sterile MECs, 63.3% of the initial toluene in the biotic MEC was removed, while it remained stable in the control. The current density increased when toluene was further spiked in the reactors. These data showed that C. metallidurans CH34 was able to degrade toluene under anaerobic conditions and to transfer electrons to a solid electrode.

HAMID REZA ZAFARANI

h.zafarani@tudelft.nl

TUDelft, OMI, the Netherlands

FABRICATION, APPLICATION AND RESPONSE TIME OF NEW NANOGAP SENSORS

Hamid Reza Zafarani, Liza Rassaei

Microelectrodes are known as useful tools in electrochemical sensing owing to their fast response time, small capacitive currents and steady-state voltammetric responses [1]. However their small surface area reduces the sensitivity especially in low analyte concentration media considering the limitations in sensitivity of electronic instrumentations [2]. Dual electrode systems, which are working based on redox cycling amplification, are good candidates to overcome these limitations. In redox cycling, one electrode is held at oxidation potential while the other electrode is held at reduction potential. In this manner the oxidized form of a redox couple, produced at one working electrode diffuses to opposing face and is reduced back to the starting material. Thus, each molecule cycles repeatedly between the electrodes and contributes a multitude of electrons to the detected current; accordingly, the signal is amplified. Most of the established designs for nanogap redox cycling devices require multiple fabrication steps of consecutive lithography, metal evaporation, sputtering and plasma etching.

We propose [3] and fabricate a new geometry for nanogap electrochemical sensors which consist of two closely spaced side-by-side electrodes which work under redox cycling conditions. Unlike previous nanogap devices, the proposed fabrication process is simpler with more control of the distance between the two electrodes and the open channel geometry of the gap reduces the response time of the device.

FABIO BOTTARI

fabio.bottari@uantwerpen.be

University of Antwerp, AXES, Belgium

SURFACE MODIFICATIONS OF BORON DOPED DIAMOND ELECTRODES: "SOFT" ELECTROCHEMICAL PRETREATMENTS IN AQUEOUS BUFFERS

F. Bottari, K. De Wael

Conductive diamond materials, like boron-doped diamond (BDD), have attracted a considerable amount of interest as electrodes in recent years. Their unique characteristics, like wide potential window in aqueous solvent, low background current, chemical inertness and physical stability are much desired for analytical and bioanalytical applications [1]. It is well reported in literature that the electrochemical behavior of the BDD electrode is determined by the surface termination as well as the boron doping level [2,3]. The electrode surface could be O-terminated (O-BDD) or H-terminated (H-BDD). This modification changes the wettability of the electrode as well as the available functional groups on the surface. Many different techniques could be employed for the pretreatment of BDD electrode, like plasma, UV irradiation or electrochemical modification. The electrochemical pretreatment could be cathodic or anodic in nature to obtain H-BDD and O-BDD electrodes respectively, and may employ various potentials and solutions. We choose to focus on two pretreatments, one anodic between 0 and +2.5V, and one cathodic between 0 and -1.7V, in phosphate buffer 0.1M, pH 2 and pH7. The aim is to understand what are the surface modifications that occurs increasing or decreasing the pretreatment time. We want to investigate the influence of both pretreatment, in term of potential windows available and redox behavior. We would like to demonstrate that even a "soft" pretreatment can dramatically changes the electrode behavior and improve the performances of the electrodes. The electrochemical activity of the BDD surface was investigated by Cyclic Voltammetry employing different redox mediator, namely $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$, while the surface was characterized by Scanning Electron Microscopy and Raman Spectroscopy.

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STEFANO LORETO

Stefano.loreto@uantwerpen.be

University of Antwerp, LADCA, Belgium

EFFECT OF THE PORE SIZE AND SURFACE PROPERTIES ON THE ELECTROCHEMICAL ACTIVITY OF GLOBIN PROTEINS INCORPORATED IN MESOPOROUS TITANIUM DIOXIDE. A COMPARATIVE STUDY

Stefano Loreto, Karolien De Wael, Vera Meynen

The development of biological sensors is currently one of the most active areas of chemical research. A biosensor is based on the electrochemical response towards the concentration of an analyte given by a sensing element (mainly proteins). The biomolecules stability and the signal transfer are key issues in the applicability of the biosensors. Mesoporous materials are ideal substrates for the incorporation and immobilizations of proteins due to their high surface area, pore volume and tunable properties. The 3-D structure and so the activity of a protein upon the incorporation inside the pores is mainly due to the interaction between the biomolecule and the pore walls. Therefore, the pore size and the surface properties, e.g. hydrophilicity and presence of organic groups, are expected to have a strong impact on the activity of the incorporated proteins. Mesoporous TiO2 could be very promising with respect to the possible joined effects of semiconductor properties and redox active proteins. However, the controlled synthesis of titanium dioxide is a challenging step due to the fast hydrolysis of the precursor, often leadings to disordered mesoporous structures and non-uniform pore networks.

We successfully synthetized highly ordered mesoporous TiO2 with a wide range of homogeneous pore size, large surface area and pore volume. Additionally, we modified the surface of the mesoporous TiO2 using propyl and 3-amino propyl phosphonic acid in order to study the impact of different organic groups on the surface. We used this material for the adsorption of horse hearth myoglobin, a globular shape heme-protein with a mean diameter of 5 nm. We studied the impact of the buffer choice, the effect of the confinement in different pores and the influence of surface functional groups (amino and methyl group) on proteins incorporation and stability. The incorporation has been monitored by UV-vis spectroscopy. The stability of the encapsulated myoglobin has been evaluated by the electrochemical activity (Cyclic Voltammetry) of the heme iron. Langmuir and Laviron model have been used to elaborate model for the adsorption and the electrochemical behavior respectively. The results clearly show the beneficial effect of the encapsulation into the pores and an influence, to some extent, of the surface modification. Although further experiments are required to extend the range of applicability of this material, the mesoporous material seems to be a promising material for biosensor development.

MICHAL KIZLING

mkizling@gmail.com

University of Warsaw, College of Inter-Faculty Individual Studies in Mathematic and Natural Sciences (MISMaP), Poland

RETICULATED VITREOUS CARBON (RVC®) AS SCAFFOLD FOR GOLD NANOPARTICLES AND ENZYME IMMOBILIZATION IN 3D - ENZYMATIC FUEL CELL DESIGN

Michał Kizling, Bartosz Olszewski, Maciej Dzwonek, Krzysztof Stolarczyk, Renata Bilewicz

The porous, conductive carbon material - reticulated vitreous carbon (RVC®), was developed 30 years ago and has been repeatedly used as a matrix for active mass and a current collector in „classical" primary and secondary batteries as well as electrode substrate for electroanalytical applications. [1] Its low density, high void volume and low resistivity make it a desirable electron-conductive foam material for batteries. Currently it is not as wide-spread as expected, although it has been demonstrated that RVC® can be covered electrochemically with a very thin layer of platinum or platinum-rhodium alloy and exhibit the behavior of a solid metal electrode.

In this report we present application of RVC® in enzymatic fuel cell technology. Due to the fact that this type of carbon is an open-pore material (20 ppi – pores per inch), the surface can be covered with particles of diameters down to ca. 100-200 nm. Also, such pore size enable close to laminar flow of solution through total volume of electrode.

In our work, cylindrical RVC electrode was ethylaminated on the surface, then gold nanoparticles modified with 4-mercaptobenbzoic acid and electroactive groups were covalently attached to the surface of the electrode through DCC coupling. Such scaffold was used for enzyme immobilization: RVC offers high real surface of the electrode. Ultra small nanoparticles anchored on the surface, due to specific electronic properties work as mediating units in the electron transfer processes. They also enable enzyme orientation on the electrode appropriate for direct electron transfer. The designed bioelectrode was employed in the enzymatic fuel cell, in which fuel solution flows directly through the whole volume of the RVC® material, in contrast to standard planar devices were it only contacts the two dimensional surface of electrode.

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RENATA BILEWICZ

bilewicz@chem.uw.edu.pl

University of Warsaw, Faculty of Chemistry, Poland

ELECTROCHEMICAL MONITORING OF DRUG RELEASE FROM LIPID CUBIC PHASES AND NANOPARTICLE CARRIERS

Renata Bilewicz, Ewa Nazaruk, Monika Szlezak, Monika Zawadzka

Bicontinuous lipidic cubic phases (LCPs) are non-toxic, biodegradable, optically transparent, thermodynamically stable in excess water, and can incorporate active molecules of any polarity. An interesting property of cubic phase is also its ability to disperse into nanoparticles called cubosomes. Cubosomes are less viscous and they can stably exist in equilibrium with aqueous solution and retain an internal bicontinuous structure. In contrary to liposomes or micelles cubosome is more resistant to mechanical or osmotic rupture. Cubic phase is employed as the carrier to protect the normal body cells from harmful effects of the drug and to stabilize the drug when it is unstable. The cubic phase nanoparticle delivery system can be used to improve the oral bioavailability of poorly water-soluble drugs. The structure and dynamics of lipidic mesophases, and their interactions with guest molecules can be tailored by applying additives, thereby achieving novel materials with improved functions for drug delivery. [1, 2]

We present lipid-liquid crystalline phases and nanoparticles as effective and safe anticancer drug delivery system. Doxorubicin (DOX), a model drug that contains an amine group and a hydrophobic part, was loaded into the cubic phase and cubosomes. The release behavior of DOX was evaluated by using electrochemistry and UV-vis spectroscopy in two buffered solutions at pH 5.5 and 7.4. pH sensitive release is crucial for a delivery system to release drugs at the target tumor cells. The investigation of the release behavior in vitro indicated that the DOX was released from nanoparticles faster at pH 5.5 than at pH 7.4. Monoolein cubic phase can be also doped with hydrophobic magnetic nanoparticles which allows to move the carrier by means of magnetic field. Release profiles of DOX from hybrid LCPs were monitored electrochemically using DPV. The addition of hydrophobic magnetic nanoparticles located in the lipidic part of the phase only slightly accelerates the drug release and therefore is useful for addressing the drug carrier.

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DEEPAK PANT

deepak.pant@vito.be

Flemish Institute for Technological Research (VITO), Separation and Conversion Technology, Belgium

RECENT ADVANCES IN BIOELECTROCHEMICAL CONVERSION OF CO2 TO CHEMICALS: ELECTROSYNTHESIS VIA BACTERIA AND ENZYMES

Research over the years has proven that generation of electric current is possible from the metabolism of organic substrates in microbial fuel cells (MFCs), with bacteria acting as electrocatalyst. By converting the chemical energy stored in organic substrates to electricity, MFCs can substantially reduce the operational cost of wastewater treatment plants, or when fully operational even achieve energy self-sufficiency. On the other hand, microbial electrolysis cells (MECs) have been used for the production of hydrogen at the cathode by providing a small amount of external electric energy. However, in recent years, a new concept of microbial electrosynthesis has been applied wherein there are same kind of setups—generally known as microbial electrochemical systems (MXCs) or bioelectrochemical systems (BES). These systems are being used for the production of chemicals using bacteria as electrocatalyst [1]. Already the bioelectrochemical reduction of carbon dioxide to acetate has been achieved [2], as well as the reduction of CO_2 to methane and multi-carbon compounds [3]. Global efforts are underway to utilize several other types of bacteria using a wide variety of substrates for production of an array of compounds. The key advantage foreseen here is the use of excess electricity that is often generated renewably such as from solar cells and wind mills, all of which cannot be utilized immediately. This excess electricity can be fed into a BES system to produce chemical compounds. We will report our first results with specific bacteria towards bioelectrochemical conversion of CO_2 to organic compounds. Acetogens like Sporomusa and Clostridium sps. were experimented for their bioelectrochemical CO_2 reduction capacity at -0.6 V vs Ag/AgCl cathode potential. Adjustment of reduction potential and optimization of cell conditions were carried out in a fed batch reactor with an activated carbon cathode. Production of 67 mg/L ethanol with mixed culture as biocatalyst was the most remarkable achievement.

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STANISLAV TRASHIN

stanislav.trashin@uantwerpen.be

University of Antwerp ,AXES, Belgium

ELECTROCHEMICAL STUDY OF HUMAN NEUROGLOBIN. MOLECULAR MECHANISM, BIOLOGICAL ROLE, AND BIOSENSING APPLICATION

Stanislav Trashin, Mats de Jong, Silvia Dewilde, Karolien De Wael

Redox proteins such as globins play crucial roles throughout the life-cycle of cells. Although oxygen binding/supply is generally accepted as the main function in penta-coordinate globins, additional roles were established in metabolism of reactive oxygen and nitrogen species. Molecular mechanisms and in-vivo roles of newly discovered hexa-coordinate globins including human neuroglobin (NGB) still puzzle researches [1]. Until now scarcely attention has been paid to electrochemical studies of NGB.

NGB was immobilized on gold electrodes using a recently developed protocol, which is based on a bis-silane precursor dissolved in pH 7 buffer without organic solvents. The immobilization protocol provided good surface coverage, fast electron transfer kinetics, and excellent electrode stability.

Detailed electrochemical studies on NGB showed that O_2 inhibits electrochemistry of the protein (−0.13 V vs SHE) while the presence of submicromolar NO can “release” the electroactive deoxy-ferrous (Fe^{+2}) NGB from the oxygenated protein even in the presence of high levels of O_2. The internal disulfide bridge regulates kinetics of NO oxidation and defines either the deoxy-NGB can appear in the presence of O_2 and submicromolar NO. NGB showed highly reversible electrochemistry and was completely stable at room temperature for at least 24 h and at 4^{o}C for at least 3 months. It opens opportunities for its further application in biosensing. Electrochemical signal of the ferrous (Fe^{+2}) NGB is suppressed in the presence of O_2 according to CrEr mechanism which can be used for calibration-free O_2 measurements in 0.1 – 10 nM or 1 - 50 nM range using one of two available NGB isoforms. Also electrochemistry of NGB is sensitive to NO concentration and can be used for NO detection in the range of concentration from 1 nM and up to 1 µM.

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NICK SLEEGERS

Nick.sleegers@uantwerpen.be

University of Antwerp, AXES, Belgium

DEVELOPMENT OF AN ELECTROCHEMICAL SCREENING STRATEGY FOR THE DETECTION OF B-LACTAM ANTIBIOTICS IN A VARIETY OF STREAMS

Nick Sleegers, Karolien De Wael

Antibiotic resistance is a global phenomenon, compromising the effective prevention and treatment of an ever-increasing range of bacterial infections. The misuse of antibiotics in humans and animals as well as unnecessary exposure in waste streams is accelerating this resistance process. Therefore, it is crucial to detect antibiotics in a fast and accurate way in a variety of streams such as milk or industrial waste water. Especially for penicillin's and cephalosporin's, both β-lactam antibiotics, which are the most commonly used antibiotics. Electrochemical sensors are very attractive for these monitoring purposes as these devices are fast, portable and extremely sensitive and selective towards their targets.

The scope of this work is the development of a portable device suitable for detection of β-lactam antibiotics in various streams. This can be achieved through the joint action of aptamers, synthetic oligonucleotides that selectively interact with the β-lactam antibiotics, combined with electrochemical detection which allows a fast, on-site and sensitive detection of low concentrations (ppb-level) of redox active species in this case the β-lactam antibiotics.

The presented and crucial step of this research is the screening and assessment of the redox behavior of these antibiotics. An oxidation response related to the base structure of both penicillin's and cephalosporin's was observed at specific potentials. Also signals related to certain specific side chains of these antibiotics were observed at a bare boron doped electrode. The interference caused by the real matrices and the presence of other antibiotics was analyzed by the preparation and examination of artificial binary samples. The electrochemical screening strategies allows us to compose the so called 'electrochemical fingerprint' of each β-lactam antibiotic. The redox properties of different β-lactam antibiotics and their production intermediates were investigated by Differential Pulse Voltammetry.

AMÉRICO G. DUARTE

americoduarte@itqb.unl.pt

ITQB-NOVA, Bacterial Energy Metabolism, Portugal

DIRECT ELECTRON TRANSFER IN THE DISSIMILATORY SULFATE REDUCTION PATHWAY

Américo G. Duarte, André A. Santos, Inês A. C. Pereira

The dissimilatory adenosine 5'-phosphosulfate reductase (AprAB) is a key enzyme in the sulfate reduction pathway that catalyzes the reversible two electron reduction of adenosine 5'-phosphosulfate (APS) to sulfite and adenosine monophosphate (AMP). The physiological electron donor for AprAB is proposed to be the conserved quinone-interacting respiratory QmoABC membrane complex, coupling the quinone-pool to sulfate reduction. However, direct electron transfer between these two proteins has never been observed. In our work, we demonstrate for the first time direct electron transfer between the Desulfovibrio desulfuricans ATCC 27774 QmoABC complex and AprAB. Cyclic voltammetry conducted with the modified Qmo electrode and AprAB in the electrolyte solution presented the Qmo electrochemical signature with two additional well-defined one electron redox processes, attributed to the AprAB catalytic center (FAD) redox behavior. Moreover, experiments performed under catalytic conditions using the QmoABC modified electrode, with AprAB and APS in solution, show a catalytic current peak develop in the cathodic wave, attributed to substrate reduction, and which is not observed in the absence of QmoABC. Substrate dependence conducted with different electrode preparations (with and without immobilized Qmo) demonstrated that the QmoABC complex is essential for efficient electron delivery to AprAB, in order to sustain catalysis. These results confirm the role of QmoABC in electron transfer to AprAB.

BIRGIT STUBBE

birgit.stubbe@ugent.be

Ghent University, PBM research group, Belgium

CYCLIC VOLTAMMETRY AS A TOOL FOR CHARACTERIZING ANTIMICROBIAL WOUND DRESSINGS WITH CONTROLLED RELEASE OF PVP-I.

Birgit Stubbe, Sandra Van Vlierberghe, Gilles Brackman, Mohaddeseh A. Aref, Henk Hoeksema, Stan Monstrey, Frank Vanhaecke, Piet Van Espen, Karolien De Wael, Tom Coenye, Peter Dubruel.

Despite the development of advanced diagnostic tools and treatments, burns are still considered a global health problem. A dressing stimulating wound healing could reduce the need for surgery, the hospitalization time and the risk of hypertrophic scarring. Therefore, the present work focuses on the development of hydrogel dressings providing a moist wound environment and antimicrobial activity by controlled release of povidone-iodine (PVP-I).

In a first step, gelatin was modified with crosslinkable moieties and hydrogel films were prepared via film casting upon the addition of a photo-initiator and the application of UV irradiation. The crosslinking kinetics and final hydrogel properties were studied using rheology, texturometry and swelling experiments.

Next, PVP-I was introduced via two different strategies: by incubating a crosslinked gelatin film in a PVP-I solution or by incubating a crosslinked film consisting of a blend of modified gelatin and PVP in an iodine solution. A calibration method was developed to allow quantification of the iodine content using XRF. Considerably higher amounts of iodine can be introduced via the second strategy. In addition, cyclic voltammetry (CV) was evaluated as well. Interestingly, CV enables to study the release of iodine from the hydrogel films by performing multiple scans consecutively. The possibility to perform CV in wound fluid mimic, a more realistic environment, was evaluated as well.

Finally, the antibacterial properties were studied in vitro using S. aureus. Agar inhibition tests show increasing antimicrobial activity upon increasing PVP-I concentration. A selection of materials produced via the second approach showed bacterial growth inhibition after 24 hours of incubation.

SANAZ PILEHVAR

Sanaz.pilehvar@uantwerpen.be

University of Antwerp, AXES, Belgium

DEVELOPMENT OF NEW STRATEGIES FOR ELECTROCHEMICAL APTASENSING

Sanaz Pilehvar

In the present study, new strategies were developed and used to achieve efficient electrochemical aptasensing of low molecular weight target compounds. The sensitive detection of small molecule pollutants is one of the key challenges for environmental monitoring and biotechnology. The main issues which were tackled were identification and improvement of different parameters affecting the quality of the ssDNA aptamer monolayer on the surface of the sensor and subsequent performance of the electrochemical aptasensing platform. In order to reach these goals, different experimental results were obtained. As a first step, a new and efficient pretreatment procedure for ssDNA immobilization on the surface of gold electrodes was developed. Taking into account the importance of ssDNA aptamer structure on its interaction with their target molecule, a new prestructuring strategy for ssDNA aptamers was developed based on the use of DNA intercalator agents such as proflavine. The effect of the developed strategies on the efficiency of the aptasensing towards CAP detection was also evaluated. The sensitivity of the impedimetric aptasensor towards CAP detection is enhanced when the above strategies are applied. In order to further improve the immobilization of ssDNA, surface modifications of gold nanoparticles were explored and a novel electrochemical aptasensing approach was proposed. In addition, the special features of multi-walled carbon nanotubes were used to construct a highly efficient electrochemical aptasensor strategy in order to detect OH-PCB in human blood serum. The MWCNTs provide a high surface area for aptamer immobilization and fast heterogeneous electron transfer. The proposed aptasensing strategies provide remarkable properties such as fast response, broad linear range, good reproducibility, acceptable stability and low detection limit.

ELENA FERAPONTOVA

elena.ferapontova@inano.au.dk

Aarhus University, Interdisciplinary Nanoscience Center (iNANO), Denmark

RATIONALIZING DESIGN OF GENOSENSORS RELYING ON ELECTRONIC PROPERTIES OF DNA

Elena E. Ferapontova

Highly specific interactions between DNA bases underlying the unique biorecognition and electronic properties of DNA allow their challenging bioelectronic and biosensor applications.1 In particular, DNA sensing technologies, exploiting differences in electrochemical properties of single stranded (ss) and double stranded (ds) DNA, provide efficient tools for genetic analysis based on DNA hybridization.2 Discrimination between ssDNA and dsDNA is then performed either through the reactions of DNA with redox indicators, capable of specific interactions with ss or dsDNAs,3 or via variations of the electrochemical signal stemming from the electrode-tethered redox-labelled DNA,4 both strongly depending on electron transfer (ET) properties of individual DNA molecules.

Here, I overview our recent studies of ET mediated by the DNA duplex, operating as a one-dimensional electronic conductor,5,6 and of ET in the redox probe-conjugated DNA duplexes triggered by the potential-induced diffusion of the redox probe to the electrode,7,8 including the ways of their optimisation by the proper choice of the DNA probes,5,9 removal of the alkanethiol linker representing an extra barrier for ET and introduction of new “minimized” linkers.6 These results allow better understanding of ET reactions proceeding in the electrode-tethered DNA and design of advanced genosensor technologies for cost-effective and efficient genosensors.

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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 at gold electrodes
3. Pulse-potential assisted post-modification of DNA-covered surfaces using alkyl thiols
4. Reading out DNA hybridization: Electrochemical impedance spectroscopy and surface enhanced Raman scattering
5. High-sensitive DNA assays based on intercalation and enzymatic amplification
6. Carbon nanoelectrodes as basis for high-sensitive H2O2 sensors
7. Oxidative stress at the single cell level detected with nanosensors
8. Field-effect transistor type nanosensors fort he local detection of pH modulation and ATP

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POSTERS

JAVAD BEHESTIAN

j.beheshtian@gmail.com

Shahid Rajaee University, Chemistry, Iran

PREPARATION AND APPLICATION OF PURE AND FE DOPED TIO2 NANOSTRUCTURES MODIFIED ELECTRODE FOR THE SENSITIVE DETERMINATION OF LEVODOPA

Javad Beheshtian, Bahram Hosseini nia, Masoumeh Ghalkhani, Azam Anaraki Firooz

In this paper, we report a simple low temperature hydrothermal method to synthesize pure TiO_2 and TiO_2 doped with 1 wt. % Fe nanoparticle. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), UV-Vis spectroscopy and photoluminescence (PL) to investigate the surface crystallographic phase, morphology and optical properties. The electrochemical response of the carbon paste electrode modified with TiO_2 and 1 wt. % Fe doped TiO_2 nanoparticles toward levodopa (L-Dopa) was studied. Cyclic voltammetry studies of L-Dopa electro-oxidation using prepared modified electrodes showed electro-catalytic properties and a significant reduction in anodic over voltage compared to the bare electrode. Under optimized experimental conditions, the best response was obtained in terms of the current enhancement, over voltage reduction, and reversibility improvement of the L-Dopa oxidation reaction by modified electrode with titanium dioxide nano particles doped with Fe.

WIOLETA BIAŁOBRZESKA

wioleta.bialobrzeska@phdstud.ug.edu.pl

University of Gdansk, Faculty of Chemistry, Department of Analytical Chemistry, Poland

THE STUDY OF INTERMOLECULAR INTERACTIONS OF 9,10-ANTHRAQUINONE WITH OXYGEN USING ELECTROCHEMICAL METHODS.

W. Białobrzeska, P. Niedziałkowski, E. Wnuk, Z. Jelinska, T. Ossowski

Anthraquinones are an important class of naturally occurring biologically active compounds. Many anticancer drugs belong to the separate group of compounds known as anthracycline antibiotics. All of these drugs have a 9,10-anthraquinone skeleton in the structure. The most popular of anthracycline antibiotics used in cancer treatment are doxorubicin and daunorubicin.

9,10-anthraquinone derivatives are compounds which play an important role in the redox processes due to the ability to form free oxygen radicals. Reactive oxygen species are chemicals which occur predominantly in cells under physiological conditions during many metabolic processes. Most of reactive oxygen species formed as a result of oxidative stress. Anthraquinone derivatives, which are an important class of anticancer drugs, possess the ability to mediate the transfer of one electron to molecular oxygen to form the superoxide anion radical, which results in their undesirable peroxidation and further cardiotoxic properties.

The aim of this study was to investigate the intermolecular interaction of selected derivatives of 9,10-anthraquinone containing piperazine and piperidine units in the structure with molecular oxygen. All compounds were examined by cyclic voltammetry (CV) in a solution of DMSO in the presence of 0.1 M $(Bu)_4N(PF_4)$. All of measurements were performed in the different concentration of oxygen and in the absence of oxygen. Obtained results directly indicate that the investigated compounds undergo of intermolecular reaction with oxygen. Additionally this results correlate with antitumor activity of examined molecules.

BIANCA CIUI

Bianca.Ciui@umfcluj.ro

"Iuliu Haţieganu" University of Medicine and Pharmacy, Analytical Chemistry Department, Romania

NOVEL GOLD NANOSTRUCTURED PLATFORMS FOR THE SENSITIVE DETECTION OF NEUROMEDIATORS

Bianca Ciui, Anca Florea, Mihaela Tertiş, Robert Săndulescu, Cecilia Cristea

Adapting electrochemical detection to multiplexed sensors systems represents one of the main approaches in biomedical research due to the wide range of envisaged applications. The immobilization method for biocompounds such as antibodies or aptamers represents the critical step towards the achievement of fast electron transfer in the fabrication of electrochemical biosensors. Their direct adsorption onto the sensing platforms is a commonly used approach, but the stability of the obtained configurations in terms of reproducibility and sensitivity is limiting potential applications. Integration of nanomaterials significantly improves the performance of related biosensors. For example, gold nanoparticles provide a high specific surface area, high conductivity and electrocatalytic activity, constituting additionally suitable immobilization sites for bioelements.

For the detection of neurotransmitters such as dopamine and serotonin, aptasensors were developed based on thiolated aptamers immobilized on gold nanostructured electrodes. To obtain a high surface area for the immobilization of aptamers, polystyrene beads were firstly deposited on the electrodes. The gold nanostructure was electrochemically obtained by gold deposition using cyclic voltammetry, followed by removal of the polystyrene beads by means of an organic solvent. Thiolated aptamers were then bound to the gold surface and the subsequent recognition and binding of neurotransmitters was evaluated. The nanostructured gold surface was further evaluated by AFM images. The obtained aptasensors were characterized by electrochemical impedance spectroscopy and by differential pulse voltammetry. Experimental parameters, such as concentration and incubation time with aptamer and incubation time with neurotransmitters, were optimized in order to find the best conditions for the aptasensor performance.

EMILY COOKSEY

emily.cooksey@manchester.ac.uk

University of Manchester, Dr Stuart Holmes, United Kingdom

MICROBIAL FUEL CELLS FOR WASTEWATER TREATMENT

Emily Cooksey; Stuart Holmes, Nigel Brown, Konstantinos Theodoropoulos

Every year billions of litres of wastewater are produced in the UK alone. Current treatment systems require either vast amounts of energy to operate or large areas of land; making them costly to implement and run. Typically these processes produce large quantities of sludge due to their aerobic nature, requiring further treatment, adding to the cost and inefficiency of the system.

Demand for water is ever increasing as well as the need to create sustainable technology, leading to a growing need for a new type of treatment. One promising alternative is the use of microbial fuel cells (MFCs). These fuel cells use bacteria to split waste material into protons and electrons through oxidation under anaerobic condition. Electrons are forced around the cell whilst protons pass through; when they re-join the products are clean water and electricity.

The long-term aim of this work is to explore the potential of MFCs for industrial use, and to design and develop a system capable of being scaled from laboratory to industrial use. One key factor that will determine the design and operation of the fuel cell is cost. To make this process industrially viable the costs need to be kept to a minimum. In order to do this, ultimately, the process is to be optimized without an expensive proton exchange membrane, without catalysts and without the use of alternative terminal electron acceptors to oxygen.

The initial experiments explore the use of a batch system comprised of a two-chamber MFC divided by a Nafion 117 membrane, containing graphite supported carbon cloth electrodes. The purpose of this system is to develop a simple model to explore properties of electrode material, bacterial culture and wastewater feed before continuing with the more complex continuous system. This will help to identify any fuel cell arrangements capable of minimizing the impact of internal resistance on the performance of cell in terms of both wastewater treatment and power generation.

MACIEJ DZWONEK

mdzwonek@chem.uw.edu.pl

University of Warsaw, Renata Bilewicz research group, Poland

SYNTHESIS AND CHARACTERIZATION OF GOLD NANOPARTICLES AND THEIR USE IN DRUG DELIVERY SYSTEMS

Maciej Dzwonek, Agnieszka Więckowska, Renata Bilewicz

Targeted therapy uses antineoplastic drugs which are attached to biologically active molecules and can selectively accumulate in the diseased tissue. A unique advantage of targeted therapy is the ability to destroy diseased tissues without damaging healthy ones. This is particularly important for small tumors at an early stage of development and small metastases. A limitation of the use of targeted therapy is the need to find appropriate receptors on tumor cells and biologically active molecules having affinity for these receptors. Gold has a high affinity for compounds containing a thiol functional group (-SH), creating the possibility of functionalization of the obtained nanoparticles and their use in the construction of electronic devices, catalytic surfaces, biofuel cells, biosensors and drug delivery systems. The advantage of gold nanoparticles is that they could have on their surface a plurality of molecules of drug or radionuclide's atoms. Targeting biomolecule anchored to a thiol group on the gold nanoparticle directly guides such systems to the appropriate receptors on the tumor cell.

In the project we describe the method for preparing small water-soluble gold nanoparticles modified with folic acid derivatives as potential targeted drug carriers for antitumor therapy. The synthetic approach relies on modified Brust-Schiffrin method using derivatives of folic acid and different PEGs to improve water-solubility of the obtained nanoparticles. Physical properties of nanoparticles were characterized by UV-Vis spectroscopy, transmission electron microscopy (TEM), and dynamic light scattering spectroscopy (DLS). The interaction between folate receptor on tumor cells and functionalized nanoparticles will be examined by surface resonance spectroscopy (SPR). Their ability of cell membrane penetration will be monitored by confocal microscopy and cytotoxity will be examined by the biological methods: MTT, Neutral Red Uptake or Anexin V affinity assays.

ALEXANDRA OANU HOSU

hosu.oana@umfcluj.ro

"Iuliu Haţieganu" University of Medicine and Pharmacy, Department of Analytical Chemistry, Romania

NEW POLY(METHYLENE BLUE) NANOSTRUCTURED FILMS FROM DEEP EUTECTIC SOLVENTS: SYNTHESIS, CHARACTERIZATION AND APPLICATION

Oana Hosu, Madalina M. Barsan, Cecilia Cristea, Robert Sandulescu, Christopher M.A. Brett

There has been increased interest in using ionic liquids as non-volatile liquid salt solvents for chemical reactions and synthesis of electroactive/conducting films with different morphologies by replacing the aqueous/organic medium with ionic liquids, during the polymerization procedure. [1] Deep eutectic solvents (DES), a new class of "green" designed solvents that offer an inexpensive, biodegradable and robust alternative to conventional ionic liquid solvents have been shown to be highly promising for the synthesis of conjugated conducting polymers, e.g. poly(3,4-ethylenedioxythiophene) [2].

New poly(methylene blue) (PMB) films have been synthesized from different deep eutectic solvents, among which ethaline and glyceline. The electropolymerization parameters and solution composition was varied in terms of pH, monomer and water content. The optimized films were electrochemically characterized by cyclic voltammetry and electrochemical impedance spectroscopy and furthermore compared with poly(methylene blue) films obtained from aqueous solution, by using a previously optimized procedure. Electrochemical quartz crystal microbalance was used to quantify the deposited film and its operational and storage stability as well as the polymerization mechanism. Surface characterization by scanning electron microscopy enables to distinguish different morphologies of the obtained PMB films from different media. Applications of the newly developed PMB modified electrodes will be presented, with emphasis on quantification of pharmaceutical formulations.

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ZOFIA JELIŃSKA

zofia.jelinska@phdstud.ug.edu.pl

University of Gdansk, Department of Analytical Chemistry, Poland

VOLTAMMETRIC DETERMINATION OF SELECTED PHARMACEUTICALS.

Zofia Jelińska, Paweł Niedziałkowski, Jacek Sein Anand, Wioleta Białobrzeska, Tadeusz Ossowski

The aim of the presented study was to prepare fast, sensitive and selective methods of detection and identification of selected painkillers commonly used around the world.

Electrochemical methods have a number of advantages like high selectivity and sensitivity or simple design of the analytical equipment. Electrochemistry could be an inexpensive tool in pharmaceutical analytics especially in case of rapid screening or complementing existing methods, and may become the primary method used in the monitoring therapy. It seems that the electrochemical properties of drugs also give a view into its pharmacokinetics and pharmacodynamics properties. It is worth mentioning that the electroanalytical techniques could be used to determinate pharmaceuticals in various materials due to analytes can be easily identified by their voltammetric potential.

In presented study, a various of electrodes, including conventional glassy carbon and a new boron doped diamond (BDD), have been used to determination of selected pharmaceuticals by cyclic and differential pulse voltammetry in different pH.

AGATA KRZAK

agata.krzak@chem.uw.edu.pl

University of Warsaw, prof. Renata Bilewicz group, Poland

THE INFLUENCE OF CYCLODEXTRIN ON THE ANTHRACYCLINE INTERACTION WITH DNA

Agata Krzak, Olga Swiech, Maciej Majdecki, Tomasz M. Stepkowski, Marcin Kruszewski, Renata Bilewicz

Daunorubicin (DNR) and doxorubicin (DOX) are anthracycline antibiotics widely used as anticancer drugs. The antitumor activity of the anthracycline is associated with the intercalation of the planar aromatic ring system between DNA base pairs and the inhibition of both DNA and RNA synthesis. The primary factor limiting full use of the anthracycline compounds are their toxic effects on the myocardium. The specific toxicity is due to generation of excess reactive oxygen species (ROS) produced in redox reactions of anthracyclines, such as Fenton reaction. The toxicity can be reduced by creating an inclusion complex between the anthracycline molecule and cyclodextrins (CD). The limitation in the use of CD as a carrier of anthracycline drugs is the low stability constant of the complex compared with that of the drug-DNA complex. However, appropriate modification of cyclodextrin can increase stability constants of the drug-CD inclusion complex. In the present study, we examine the stability constant of modified CD-DNR or DOX complexes in physiological pH 7.4 and at pH 5.5 (characteristic for pathologically changed cells). Electrochemical studies revealed that at pH 7.4 the modified CD-drug complexes are stronger than at pH 5.5. We investigate the effects of the modified CD-drug complex on the anthracycline interaction with DNA. Voltammetric and spectroscopic studies show that modification of CD with the antioxidant - lipoic acid, leads to an increase of drug affinity towards DNA. Moreover, confocal microscopy studies on HeLa cells show that the modified CD-DNR complex significantly increase efficacy of the therapy compared with that of the free drug.

ELENE KVARATSKHELIA

elicko@mail.ru

Iv. Javakhishvili Tbilisi State University , R.Agladze Institute of Inorganic Chemistry and Electrochemistry, Georgia

THE ELECTROLYTIC DISSOCIATION OF ETHYL DERIVATIVES OF SUCCINIC ACIDS

Elene Kvaratskhelia, Rusudan Kurtanidze

Succinic acid and its various derivatives are widely used in the organic synthesis and polymer industry, participate in the biologically important Krebs cycle. In this work an analysis of the regularities of the electrolytic dissociation of DL-2,3-diethylsuccinic and meso-2,3-diethylsuccinic acids in their dilute (0.0001-0.01M) solutions was carried out with the aid of a new method of determination the dissociation parameters of weak multibasic organic acids with the “overlapping” equilibria previously described by authors. Values of the usual and “partial” degrees of dissociation, the concentrations of all anions, hydrogen ions and undissociated acid molecules, the activity coefficients of all charged dissociation products were calculated. Together with the accurate equations were also suggested the simple empirical equations for fast approximate determination of the various dissociation parameters.

WIOLETTA LWIŃSKA

wchmielowiec@chem.uw.edu.pl

Faculty of Chemistry, University of Warsaw, Laboratory of Theory and Applications of Electrodes, Poland

ENVIRONMENTALLY SENSITIVE NANOHYDROGELS WITH TRI-SEGMENT OLIGONUCLEOTIDE HYBRIDIZATION FOR PROLONGED RELEASE OF DRUGS-INTERCALATORS

Wioletta Liwinska

Recent interest in the field of nano-sized drug delivery systems, in strategies of its pre-formulation and formulation, is among others focused on creation of the systems for poorly soluble and/or highly unstable substances/drugs. It became a significant area in pharmaceutical research. Polymer and hydrogel-based materials with incorporated oligonucleotides are recently often selected as particularly promising substrates for design of delivery systems. These materials have been successfully used in several biomedical applications due to their unique dynamical structural properties such as: complementarity, denaturation, annealing, hybridization and conformation change.

In our work, we concentrated on the synthesis and optimization of nanogels built of PNIPA and AAc monomers. DNA oligonucleotides were attached to the polymer chains for improved delivery of selected anticancer drug – Dox. The nanogels were synthesized using the free radical polymerization method. The acrylic groups were present in two independent DNA strands (oligo1 and oligo2) and in hydrogel monomers. Additionally, we used the third DNA strand, sequentially complementary to both: oligo1 and oligo2 strands. Finally the specific trisegment hybridization between two DNA strands attached to nanogels network and the third strand was achieved.

The physicochemical parameters of the novel nanoparticles, including amount of incorporated DNA, size, zeta potential and environmental sensitiveness, all referred to the volume phase transition of nanogels at increased temperature, were tested. The main goal of the investigations was to test the ability of examined networks to effective storing and prolonged release of doxorubicin. We noticed that the performance of storing and releasing of Dox was correlated with two processes: the structural change of oligonucleotides and volume phase transition of the hydrogel lattices. The change in temperature is routinely used in hyperthermia cancer treatment.

MEHDI NEEK-AMAL

mehdi.neek-amal@uantwerpen.be

University of Antwerp, Physics department, Belgium

EXPERIMENTAL STUDY OF SNO2 DOPED WITH FE NANOSTRUCTURES MODIFIED CARBON PASTE ELECTRODE FOR THE SENSITIVE ELECTROCHEMICAL DETECTION OF LEVODOPA

Mehdi Neek-Amal, Javad Beheshtian

In this study, undoped SnO2, nanostructures and 1 wt.% doped with Fe nanostructures were synthesized by hydrothermal method. Characterization of nanostructures synthesized, has been performed by X-ray diffraction (XRD), scanning electron microscopy (SEM). The morphology of nanostructures was characterized by Scanning Electron Microscope (SEM). For investigation of optical properties, PL and UV-Vis spectrum were taken. In this thesis, the electrochemical response of the carbon paste electrode modified with synthesized nanostructures (undoped and also doped with Fe nanoparticle) toward levodopa (L-Dopa) was studied. Studies of cyclic voltammetry using provided modified electrodes showed electro catalytic properties for electro-oxidation of L-Dopa and a significant reduction was observed in anodic over voltage compared to bare electrode. Obtained results indicated the presence of the sufficient dopants. Best response was obtained in terms of the current enhancement, overvoltage reduction, and reversibility improvement of the L-Dopa oxidation reaction under experimental conditions by modified electrode with SnO2 nanoparticles doped with iron.

VANOUSHEH RAHEMI

vanousheh.rahemi@uantwerpen.be

University of Antwerp, AXES, Belgium

UNIQUE OPTO-ELECTRONIC STRUCTURE AND PHOTO REDUCTION PROPERTIES OF SULFUR DOPED LEAD CHROMATES EXPLAINING THEIR INSTABILITY

V. Rahemi, N. Sarmadian, W. Anaf, K. Janssens, D. Lamoen, B. Partoens and K. De Wael*

Chrome yellow refers to a group of synthetic inorganic pigments that became popular as an artist's material from the second quarter of the 19th century. The color of the pigment, in which the chromate ion acts as a chromophore, is related to its chemical composition ($PbCr_1$-xS_xO_4, with $0 \leq x \leq 0.8$) and crystalline structure (monoclinic/orthorhombic). These pigments show remarkable signs of degradation after limited time periods. This degradation is assumed to be related to the reduction of Cr(VI) to Cr(III). First-principles density functional theory calculations show that both the absorption coefficient and reflection coefficients of the lead chromates change as a result of the sulfate doping in such a way that the generation of electron-hole pairs under illumination relative to the total Cr content increases. These changes in the material properties explain why paler shade yellow colors of this pigment are more prone to discoloration. The electronic structure calculations also demonstrate that lead chromate and its co-precipitates are p-type semiconductors, which explains the observed reduction reaction. As understanding this phenomenon is valuable in the field of cultural heritage, this study is the first joint action of photo-electrochemical measurements and first-principles calculations to approve the higher tendency of sulfur-rich lead chromates to darken.

JAVIER ROMÁN

javier.romansilva@gmail.com

Pontificia Universidad Católica de Valparaíso, Laboratorio de Electroquímica, Chile

STUDY ABOUT INFLUENCE OF CDTE QUANTUM DOTS IN THE OVERALL ADHESION-SPREADING PROCESS OF LIPOSOMES ON A GOLD ELECTRODE.

Javier Román, Emilio Navarrete, Eduardo Muñoz

The utilization of quantum dots (QDs) it has been grown up into different areas because they have particular optical and electronic properties. Their properties are dependent on the particle size, which can be controlled by the modification of experimental conditions: temperature, reaction time, pH and molar ratio of precursors. These properties have allowed its application in photovoltaic cells, biosensors and biomarkers. Particularly in the medicine field is very important to know the effect of QDs in contact with cell membranes. An approach is the use of lipid vesicles or liposomes, which also can be used as drug and biomarkers carriers. Some authors have used electrochemical methods in the study of liposomes, because the vesicles adhesion-spreading processes on metallic electrodes are similar to the lipid membranes fusion. This work is related with the influence of the interaction between CdTe QDs and DMPC vesicles on the overall adhesion-spreading processes of liposomes. Synthesis of CdTe QDs was carried out in aqueous media using a Doehlert's experimental design to control the QDs sizes. QDs were characterized by UV-Vis spectroscopy, cyclic voltammetry (CV) and EIS. DMPC liposomes were prepared by dissolving DMPC in chloroform, then evaporating solvent and suspending the lipids in buffer. Lipid suspension was cooled with liquid nitrogen and then heated and extruded. After, the DMPC liposomes were deposited on a gold electrode and characterized by CV observing the coverage degree. Additionally, the overall adhesion-spreading process of liposomes on gold electrode was characterized by chronoamperometry technique analyzing the current-time transients. Both analysis were performed after the mixing with CdTe QDs. The results show a decrease in the constant rate values of the adhesion-spreading processes of DMPC liposomes on gold electrode suggesting that the interaction CdTe-DMPC produces an increase in the activation energy of the lipid membranes fusion.

MIHAELA TERTIS

mihaela_tso@yahoo.com

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

MOLECULARLY IMPRINTED POLYMER BASED PLATFORM FOR THE ELECTROCHEMICAL DETERMINATION OF DOPAMINE

Mihaela Tertiș, Anca Florea, Robert Săndulescu, Cecilia Cristea

The molecularly imprinting of the synthetic polymers is increasingly used in a wide range of fields, during the last decades. Molecularly imprinted polymers (MIPs) were successfully used in applications dealing with the selective molecular binding, as they are fully artificial macromolecular structures with biomimetic properties that are able to simulate the receptor-ligand, antibody-antigen, or enzyme-substrate biorecognition processes [1]. Among the advantages of using MIPs in the place of biological compounds are included: their low cost, ease of preparation, high stability and mechanical strength, chemical and thermal stability in various conditions, etc. [2]. Presenting molecular recognition sites complementary in size, shape and chemical functionality with the target molecule, MIPs allow the achievement of hybrid materials by inclusion of a large variety of nanomaterials, such as graphene, CNTs or gold nanoparticles (AuNPs) which add unique and valuables properties [3].
A novel MIP electrochemical sensor was elaborated based on glassy carbon electrodes modified with AuNPs and tested for dopamine determination. The Au nano-film was electrochemical generated from HAuCl4 solution in H_2SO_4 to allow the self-assembly of p-aminothiophenol (PATP), on the electrode through Au-S bonds. After this step, the template was assembled onto the PATP monolayer followed by the electrochemical generation of the MIP, simultaneously with the Au framework.
CV, EIS and AFM tests were performed in order to reveal the morphological properties and for the complete electrochemical characterization of the sensor. By using DPV the developed sensor shows good sensitivity, selectivity and reproducibility for the dopamine detection from various matrices.

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SARANYA THIRUVOTTRIYUR SHANMUGAM

sarashanmugam@gmail.com

SRM University, Department of Nanotechnology, India

NOVEL AMPEROMETRIC NANOBIOSENSOR FOR FORENSIC APPLICATION – ESTIMATION OF TIME SINCE DEATH

Saranya Shanmugam, Kavitha Thandavan, Swaminathan Sethuraman, Uma Maheswari Krishnan

Enzymatic sensors would be an effective alternative to the conventional techniques owing to their specificity for determining the time since death. The present work deals with diamine oxidase immobilized on nanoparticles for quantifying the amount of putrescine. The diamine putrescine is synthesized in the body during the putrefaction process and can be converted in the presence of diamine oxidase (DAO) to hydrogen peroxide. This reaction can be sensed using electrochemical techniques which forms the basis of this work. Iron oxide (Fe_3O_4) nanoparticles synthesized using thermal co-precipitation was chosen for immobilization of diamine oxidase due to its simple preparation procedure, cost effectiveness, high surface area and biocompatibility. The enzyme was linked covalently by carbodiimide activation and characterized using FT-IR, FE-SEM and XRD. The size of the particles was in the range of 25-35 nm. For detecting the hydrogen peroxide released, a glassy carbon working electrode coated with enzyme linked iron oxide nanoparticles was poised at +0.4V versus the Ag / AgCl reference electrode. Platinum wire was used as the counter electrode. A step-wise increase in current was observed and it was linear in the range of 0.95–8.55nM and the response time was found to be less than 0.5 seconds. Amperommetric i-t curve was plotted for the estimation of diamines in the fish Channa striatus. We believe this concept can be used effectively to determine the time since death.

ALEXANDRA VERHAVEN

averhave@ulb.ac.be

Université Libre de Bruxelles, Chimie Analytique et Chimie des Interfaces, Belgium

STUDY OF DNA MIXED SELF-ASSEMBLED MONOLAYERS ON GOLD BY ELECTROCHEMICAL IN SITU FLUORESCENCE MICROSCOPY

Alexandra Verhaven, Dan Bizzotto, Thomas Doneux, Claudine Buess-Herman

The formation of well-ordered and homogeneous self-assembled monolayers (SAMs) is of great interest to the development of new biosensors. Increasingly homogeneous surfaces improve the efficiency of the recognition process. The characteristics of such surfaces are usually provided by techniques giving surface-averaged information. However, by coupling electrochemical and spectroscopic methods, one can obtain spatially resolved and/or molecular information about the SAMs.
In this work, we present a technique coupling electrochemical measurements with in situ fluorescence microscopy. This setup permits us to measure the variations in fluorescence intensity and capacity associated with the applied potential in real time.
The SAMs presently studied are composed of DNA co-adsorbed with a mercaptohexanol diluent. The DNA sequence, a 22-mer oligonucleotide, is anchored to the gold surface by the means of an alkylthiol chain in 5'. While the 3' extremity of the DNA strand is labeled with a BODIPY fluorophore.
In situ fluorescence microscopy measurements under electrochemical control were performed for various SAMs with different surface coverages. Changes in DNA orientation caused by potential perturbations were monitored providing information regarding the extent of orientation change. Moreover, the reductive desorption of SAMs were studied by capacitance and fluorescence intensity measurements. Surface coverage of the electrode was determined by chronocoulometry measurements using the electroactive hexaammineruthenium (III) marker.

URSZULA E. WAWRZYNIAK

uwawrzyniak@ch.pw.edu.pl

Warsaw University of Technology, Chemical Sensors Research Group, Poland

ALZHEIMER'S AMYLOID B-PEPTIDES OF VARYING CHAIN LENGTHS AND THEIR COMPLEXES WITH COPPER(II) – STUDIES ON REDOX ACTIVITIES

Urszula E. Wawrzyniak, Magdalena Z. Wiloch, Arkadiusz Bonna, Wojciech Bal, Simon C. Drew , Wojciech Wróblewski

Alzheimer's disease (AD) is a neurodegenerative disorder characterized by progressive cognitive decline and loss of memory. One of the pathological hallmarks of AD is the deposition of amyloid-β peptides (Aβ) of different length in senile plaques in the brain [1]. Although the electrochemical studies were mainly focused on the characterization of redox properties of Cu(II)-Aβ(1-x) complexes, recent reports pointed out the presence of a second naturally occurring dominant form Aβ(4-42) [2]. Aβ(4-42) contains the high affinity amino terminal copper and nickel motif (ATCUN), therefore distinct electrochemical behavior of Cu(II)-Aβ(4-42), a soluble model fragment of Aβ(4-42), have been expected.
The main goal of this work was to compare the redox activity of copper(II) complexes formed at physiological pH with Aβ peptides of varying lengths [Aβ(1-16) and N-truncated Aβ(4-x), where (x = 6, 8 or 10). The influence of the peptide sequence and peptide to copper molar ratio on the redox properties of the obtained structures were investigated and discussed. Voltammetry studies on Cu(II)-Aβ(4-x) complexes was carried out to reveal the differences between Cu(II) ion binding by oligopeptides possessing one or two binding sites. The reversibility of the studied redox processes in Cu(II) complexes with Aβ(4-x) derivatives was also investigated. The results indicated the crucial role of tyrosine located in the 10th position of the N terminal peptide chain in the electrochemical process of the Aβ(4-x) complex, including the removal of reversibility of the Cu(II)/Cu(III) redox couple.

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