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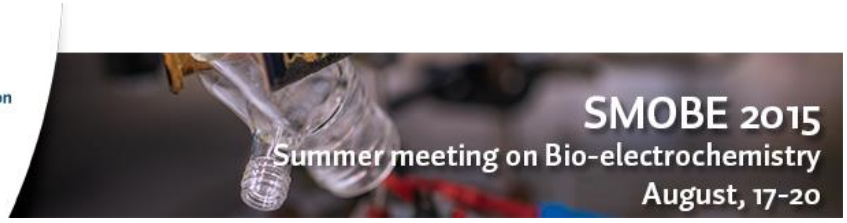

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ABSTRACTS

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KEYNOTE LECTURES

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A QUANTITATIVE USE OF FUNDAMENTAL ELECTROCHEMICAL TECHNIQUES TO STUDY BIO-ELECTROCHEMICAL SYSTEMS: FROM EXPERIMENTS TO MODELLING

Electrochemistry has undergone significant transformations in the last few decades. This evolution is due to a number of factors, but principally because of the possibility of carrying out reproducible, dynamic experiments under an ever-increasing variety of conditions with reliable and sensitive instrumentation. This has enabled many studies of a fundamental and applied nature to be carried out.

Nevertheless, in the present economic climate, it is no longer possible to only use expensive trial and error methods based on a huge number of experimental data. Instead, a profound insight in the electrochemical phenomena is required. The latter kind of knowledge can solely be obtained if the electrochemical process can be modelled in an accurate and reliable way. However, reliable modelling results are only provided when correct experimental data are available and when it can be evaluated whether the model is able to describe the experiments within the experimental error.

To tackle this problem, this presentation will give an insight in the fundamentals of three well-known electrochemical techniques: linear sweep voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Special attention will be given to an adequate data acquisition method and data quality check (importance of different measurement parameters and possible pitfalls). Hence, the data quality can be assessed and the experimental error quantified since this is a prerequisite for a robust modelling afterwards.

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BIOELECTROCHEMICAL SYSTEMS: THE NEW PARADIGM FOR ENERGY RECOVERY AND CHEMICAL PRODUCTION

Bioelectrochemical systems (BES) are hybrid devices that integrate fuel cell and microbial metabolism in single device to generate the energy and chemicals from wide spectrum of substrates. A typical BES consists of an anode chamber and a cathode chamber sheltering for oxidation and reduction reactions respectively. Several applications of BES are found and the research in this field is growing at a rapid rate towards commercialization. Microbial fuel cells (MFCs), microbial electrolysis cells (MECs), microbial desalination cells (MDCs) are most known applications of the BES. Among these, MFCs were considered as the prototype or standard BES system that treats wide varieties of organic matter in anode with the bacteria residing on anode and generates electrons and protons. The electrons and protons travel to cathode, respectively through external circuit and proton exchange membrane to reduce terminal electron acceptor to generate electricity. This basic mechanism is dealing with the several types of BES systems and the biocatalyst, substrate and the terminal electron acceptor are determining its applications. MFCs converts virtually unlimited spectrum of organic matter into bioelectricity and the organic can be from several types of waste streams. Besides bioelectricity generation, this process also benefits, in terms of oxidation of organic content in waste. In MECs, hydrogen is the major product that generates in cathode chamber from the energy equivalents generated from the electrolysis of water/organic matter in anode. Further, this principle is upgraded to produce various chemicals at cathode and the process is called as the microbial electrosynthesis (MES). MES facilitates to fix the atmospheric CO_2 to organic molecules or chemicals such as acetate, butyrate, butanol, ethanol, methanol etc. In addition to anode and cathode chambers, MDCs consists of a middle-desalination chamber additionally. It works for the removals of dissolved salts from the saline and hypersaline wastewaters along with bioelectricity generation. All the applications of BES technology are focused on the energy and value added chemicals from the waste streams and industrial emissions (CO_2) which presents a paradigm shift of industrial development to sustainable and renewable energy generating way.

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ELECTRO-ENZYMOLOGY: ELECTROCHEMISTRY OF REDOX PROTEINS AND ENZYMES

I will give a practical outline why and how to study redox proteins and enzymes with electrochemical methods. I will address how to optimize experimental parameters such as solution composition, current/voltage/time settings and methods, mass transport and cell geometry for both electrochemistry and enzymology. A critical point is how to render the electrode surface bio-compatible, either to immobilize the protein or to achieve ideal diffusion behaviour. 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. Thus, with the help of direct data analysis, and if needed also mathematical modelling and simulations (for which I will present a general outline of ingredients), biochemically relevant information can be derived from the current/voltage/time traces. Using examples, I will illustrate how the electro-enzymological experiments relate to classical cuvette activity assays, and how the multi-dimensional parameter space, with added potential dimension, can reveal new enzyme mechanistic information.

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ELECTROCHEMISTRY AND NUCLEIC ACIDS: BIOPHYSICS, NANOTECHNOLOGY, BIOSENSING

More than sixty years after the elucidation of the double helix structure of DNA, nucleic acids remain a fascinating object of scientific excitement and a source of breakthrough technologies. In the meantime, it has been realised that the Watson-Crick double-helix (so-called "canonical DNA" or "B-DNA") and the underlying H-bond pattern (A=T; C≡G) are only one case among numerous structural features exhibited by nucleic acids. Non-canonical structures encompass A-DNA, Z-DNA, triplexes, G-quadruplexes, i-motifs, hairpins, three-way junctions..., some of them involving Hoogsteen hydrogen bonds rather than Watson-Crick base pairing.

Electrochemistry is an ideal tool to study nucleic acids. Indeed, nucleic acids are polyelectrolytes, meaning that charges and electric fields -the key quantities of electrochemists- are of utmost importance in the biophysics of nucleic acids. In addition, nucleic bases can be reduced or oxidised at various electrodes, and many synthetic ligands, including intercalators, are also electroactive.

After providing a non-exhaustive overview of the above-mentioned topics involving electrochemistry and nucleic acids, this communication will focus on some specific works 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.

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RECENT ADVANCES IN CARBON ELECTRODES FOR THE DEVELOPMENT OF ENZYME-BASED BIOFUEL CELL

In this presentation, recent developments in enzymatic biofuel cell (EBFC) technology using porous carbon materials are summarized. A general introduction to EBFCs, including their operating principles and applications, the electron transfer mechanism, mediator and enzyme materials (anode and cathode) will also be provided. EBFCs are promising for sustainable green energy applications; however, they are still at an early stage of development, with many yet-to-be-resolved fundamental scientific and engineering problems. Two critical problems are short lifetime and poor power density, both of which are related to enzyme stability, electron transfer rate, and enzyme loading. To achieve the practical application of EBFCs, a promising approach is to use porous carbon materials. Strategies for the designing of hierarchically structured supports composed of mesoporous and macroporous are considered. The large surface area of these mesoporous materials can increase the enzyme loading and electron transfer efficiency. The macropores enable the efficient biocatalyst and fuel transport. The essential properties of the resulting materials with respect to the EBFC application are also discussed. A combination of electron transfer technology and porous carbon material would be helpful in achieving a much higher and stable current output, thus contributing to a practical advance in the sustainable energy field.

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BIODETECTION AT MICRO/NANOSCALE

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 catalyses 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.

FUNDAMENTALS OF ELECTROCHEMISTRY, TECHNICAL AND BIO-ELECTROCHEMICAL ENGINEERING

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ENGINEERING BIOELECTROCHEMICAL REACTORS FOR NITRATE TREATMENT

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The removal of nitrates (i.e. denitrification) of polluted waters using bioelectrochemical systems (BES) has attracted the interest of the scientific community. Relevant knowledge has been obtained on reactor operation, microbiome and thermodynamics of denitrifying-BES at lab-scale. However, the overall reactor geometry and the anode compartment function (anode electron donor and material) should be optimised before validating the technology at pilot-scale.

Here we report the denitrifying-BES performance in three different reactor geometries: i) rectangular (0.5L net cathode volume (NCC); ii) tubular L-shaped (0.25L NCC) and tubular I-shaped (1.5L NCC). In all reactors, anode and cathode were separated by a cation exchange membrane and the cathode was filled with granular graphite and poised at -320mV vs. Ag/AgCl (Pous et al., 2015). Three different anode materials (granular graphite, stainless steel and Ti-MMO) and anode electron donors (acetate, water and chloride) were evaluated. All reactors were fed with nitrate-polluted water (33mg N-NO3-/L).

Tests for optimizing the anode compartment function suggested the use of different materials depending on water characteristics (available anode electron donors). In waters containing organic matter, the use of a bioanode supported with granular graphite would be suitable. While in waters without organic matter (as groundwater), the use Ti-MMO anodes would allow a safe and sustainable water treatment without requirement of external chemicals and with potential free chlorine production.

The use of different reactor geometries revealed that denitrifying performances in tubular reactors (up to 0.7 kgN•m-3•d-1) were higher than in rectangular reactors (up to 0.1 kgN•m-3•d-1). Such an increase was related to higher reactor homogeneity and lower pH gradients.

Throughout this communication we want to highlight that BES capabilities can be highly increased for real applications by optimizing the whole system.

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RAPID MEASUREMENT OF AB CLEARANCE FROM THE BRAIN INTERSTITIAL FLUID IN MICE USING MICRO-IMMUNOELECTRODES.

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The accumulation of amyloid-β peptide (Aβ) in the brain is an initiating factor in the pathogenesis of Alzheimer's disease (AD). High concentrations of Aβ promote aggregation in the extracellular space. Clearance of Aβ from the brain is impaired in individuals with AD. Several mechanisms involved in Aβ clearance have been identified, and some of these mechanisms may be fast-acting and are unavailable to measure using currently available tools. We have recently developed a novel microimmuno-microelectrode (MIE) to detect brain ISF Aβ every 60 seconds in living mice, using square wave voltammetry. This new technique provides the temporal resolution necessary to assess very rapid changes in Aβ elimination in living mice. In our design, specificity is achieved by using anti-Aβ antibodies immobilized to the electrode surface. Anti-Aβ antibodies capture/bind Aβ molecules to the MIE surface and decrease the electron tunnelling distance between the MIE and Aβ molecules. MIEs are prepared similar to our previously described methods (Prabhulkar et al., 2012). Activation of carboxylic groups on the carbon fiber surface is achieved by application of EDC/NHSS to form a semi-stable reactive amine NHS ester. The activated microelectrodes are placed in a solution of anti-Aβ antibody (mHJ2). Following antibody attachment, MIEs are incubated with 0.05 % ethanolamine to block reactive NHS sites then 0.1% BSA to block any non-specific protein binding sites. We are using MIEs to determine the rapid kinetics of protein elimination in mice that have suppressed clearance mechanisms. By using a combination of pharmacological and genetic inhibition of proteases and transporters we can assess how these different clearance pathways act in synergy on Aβ. Using the MIEs, we can demonstrate that the elimination half-life of ISF Aβ in vivo is very short (t½ = 24 minutes). This tool can be used to assess the fast-acting clearance mechanisms in the brain of living AD transgenic mice.

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MULTIPLE SCANNING ELECTROCHEMICAL MICROSCOPY MAPPING OF TYROSINASE IN MICRO-CONTACT PRINTED FRUIT SAMPLES ON POLYVINYLIDENE FLUORIDE MEMBRANE

Tzu-En Lin, Andreas Lesch, Fernando Cortés-Salazar, Alexandra Bondarenko, and Hubert H. Girault

We introduce three orthogonal and compatible methods for detecting tyrosinase, a key factor in fruit browning and skin disorders by scanning electrochemical microscopy (SECM). All methods are performed subsequently on the same substrate area providing a wide range of relevant information. The first SECM approach that relies on the mapping of a differential pore oxygen concentration induced by the local hydrophobic changes that the adsorption of tyrosinase generates on a porous polyvinylidene fluoride (PVDF) membrane. The second approach is based on the direct monitoring of the enzymatic activity of tyrosinase by detecting amperometrically the reaction products from the enzymatic conversion of L-3,4-dihydroxyphenylalanine (L-DOPA). Finally, tyrosinase was visualized implementing a sandwich immunoassay. The multiple SECM detection strategies were successfully applied to map unequivocally the tyrosinase enzymatic activity of a micro-contact printed banana sample. Furthermore, differential pulse voltammetry and mass spectrometry analyses were employed to elucidate the nature of the electrochemical response obtained during the tyrosinase enzymatic activity experiments.

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MULTICOMPONENT POLYMER / DNA NANOFIBERS AND NANOPARTICLES FOR IMPROVED STORING AND RELEASE OF INTERCALATORS

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Recent interest in designing micro- and nano-size drug delivery systems and in strategies of their pre-formulation and formulation is oriented on creation of delivery systems for poorly soluble and/or highly unstable substances. In our work we would like to expand the synthesis ways and optimization steps needed for preparation of multicomponent drug delivery system with improved delivery properties.

The first way of synthesis involves the application of charge controlled coaxial core-shell electrospinning process for creation of thin micro- and nanocomposites of PLC/PNIPA/DNA/Au NPs with attached selected antitumor drug – doxorubicin. Doxorubicin (Dox) was attached by covalent bonding sensitive to tumour environment. Modified gold nanoparticles were entrapped in PLCL fibers during electrospinning process. We investigated the release profiles of Dox-modified Au NPs from PLC nanofibers, by spectroscopic (UV-Vis, CD) and electrochemical techniques (CV, SWV) and in vitro experiments (HeLa, Insulinoma and Glioma cells). The morphology of composites was inspected by TEM, SEM and optical microscopy.

Second way assume the introduction of particular conformations of selected aptamers into PAM and PNIPA hydrogel networks, for formation of multicomponent nanoparticles and storing of Dox and releasing of it after initiation of structural changes of aptamers and volume phase transition of lattices. Second kind of lattices was synthesized with Au NPs with attached Dox. The DNA-based biomaterials were characterized by a strong increase in guanine and adenine anodic currents that starts at physiological temperature. The structural alterations were used as a control element in the releasing of doxorubicin. Doxorubicin was slowly released by using a minor temperature increase as it is routinely done in hyperthermia. The binding strength, the rate of release of Dox and the composite properties were examined using voltammetry, SEM and ICP-MS.

BIO-ELECTROCHEMISTRY: DNA/PROTEINS

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COVALENT ATTACHMENT OF NANOPARTICLES ON GLASSY CARBON SUPPORTS AS A TEMPLATE FOR THE APTASENSING OF OFLOXACIN

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A highly sensitive and specific electrochemical aptasensor based on a target-binding aptamer as molecular recognition element was developed for determination of Ofloxacin (OFL). The signal amplification was achieved by using gold nanoparticles (AuNPs), which was covalently attached to the surface of a glassy carbon electrode (GCE), as a platform for the immobilization of the thiolated aptamer. In addition, a novel pretreatment procedure for glassy carbon electrode has been developed for efficient deposition of AuNPs on the surface of the electrode. The fabrication process of the aptasensing platform was characterized by X-ray photoelectron spectroscopy (XPS) and Electrochemical Impedance Spectroscopy (EIS) and scanning electron microscopy (SEM). In the presence of OFL molecules, the aptamer interact with OFL and folded to a complex structure. As a result, the conformational change leads to the change in electron transfer efficiency and change in the peak current. The peak current was detected by differential pulse voltammetry and cyclic voltammetry techniques. Under the optimized experimental conditions, the increase of the peak current response of the aptasensor has a linear relationship with the concentration of OFL ranging from 5E-8-2E-5 with a detection limit of 1E-9 M. The presence of other antibiotics such as Chloramphenicol and Pefloxacin did not affect the detection of OFL, which suggests a high specificity of the proposed aptasensor.

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ELECTROCHEMICAL AND IN SITU FLUORESCENCE MICROSCOPY STUDY OF THE INTERFACIAL BEHAVIOR OF A P53 PEPTIDE APTAMER SELF-ASSEMBLED ON GOLD

Eléonore Triffaux, Thomas Doneux, Dan Bizzotto, Philippe Leclère, Claudine Buess Herman

The achievement of well-ordered and homogeneous self-assembled monolayers is of major interest in the design of biosensors. Many works are devoted to study and optimise the organisation arising from the assembly. While conventional electrochemical techniques provide surface-averaged information, the use of spectroscopic methods under potential control enables obtaining spatially resolved and/or molecular information about the SAMs.

In this work, we present a unique in situ electrofluorescence microscopy technique, which is a combination of epifluorescence microscopy and electrochemical methods, performed in a specially designed setup.

The interest of such coupling for the investigation of electrochemical interfaces is illustrated by our work on the behaviour of a peptide aptamer self-assembled on gold. A peptide aptamer is an artificial peptide sequence showing a strong ability to bind the target protein with high affinity and specificity. This new class of artificial affinity probes is designed to replace antibodies as biorecognition probes in biosensors.

The aptamer sequence is based on the recognition domain of the p53 protein against the protein Mdm2. It consists of the residues 12-26 of p53, with an additional cysteine at the N-terminal to allow a covalent bonding between the sulphur and the gold surface. For microscopy purpose, the initial probe has been extended by 3 amino-acids and modified by the carboxyfluorescein fluorescent label.

Electrochemical and in situ microscopy under potential control characterisations are performed for various p53 aptamer SAMs, consisting of the aptamer alone or coadsorbed with a diluent. Electrochemical results obtained by cyclic voltammetry, impedance spectroscopy in the presence of [Fe(CN)6]3-/4- and chronocoulometry in the presence of [Ru(NH3)6]3+are discussed together with the in situ fluorescence data. Further characterisation of the SAMs by AFM measurements have also been realised.

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HIGHLY CONTROLLED AND FAST POTENTIAL-ASSISTED SSDNA IMMOBILIZATION

Daliborka Jambrec, Magdalena Gebala, Fabio La Mantia, Wolfgang Schuhmann

DNA hybridization process, and with this important DNA sensor characteristics such as sensitivity, reproducibility and the overall efficiency, greatly depend on the amount of the ssDNA on the electrode surface. Thus, well defined, reproducible and controlled DNA-modified surfaces are a prerequisite for the development of optimized DNA sensors.

Recently, the manipulation of DNA in the vicinity of electrified interfaces by means of a pulse-type modulation of the potential applied to the electrode surface is attracting increasing attention [1]. Potentials more positive than the potential of zero charge (pzc) are reported to invoke a bending of the grafted DNA towards the surface and oppositely negative potentials favour an upright orientation of the immobilized DNA strands [2]. Furthermore, previous attempts aiming on the potential-assisted DNA immobilization itself, which took pzc into consideration, referred to the pzc of the bare electrode [3]. It was reported, that due to the applied potential the DNA strands are attracted or repelled during the course of the immobilization process.

We propose a new model for the potential-assisted immobilization of DNA at gold electrodes that considers the role of counter-ions surrounding the DNA, the distance from the electrode surface to which applied potentials have effect and the shift of the pzc during the course of the immobilization due to the surface modification with DNA. Furthermore, we introduce a new and highly reproducible potential-assisted immobilization method that is much more efficient and much faster than the standard incubation method. It is based on fast switching between carefully selected potentials with respect to the pzc taking into account the change in pzc during the immobilization process.

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PORTABLE FINGER-TIP AMPEROMETRIC APTASENSOR FOR FAST, SELECTIVE AND SENSITIVE ON-SITE DETECTION OF COCAINE

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Aptamers - synthetic oligonucleotides also known as "artificial antibodies" - offer great potential for the design of biosensors with high selectivity for a given target. Electrochemistry allows a fast, onsite and sensitive detection of low concentrations of redox active targets. A joint action of aptamers and electrochemistry results in so-called electrochemical aptasensing devices able to sense target molecules with high selectivity and sensitivity. Electrochemical aptasensors are very attractive for monitoring the presence of micro traces of drugs of abuse as they are fast, portable, extremely sensitive and selective towards target molecules.

In this work, the first results will be presented concerning the development of a device suitable for cocaine detection, implemented into a finger-tip glove sensor for on-site use, with a minimum amount of equipment. Cocaine is one of the most abundant and dangerous drugs entering Belgium for local use or distribution over entire Europe and should therefore be detected in a fast and efficient way by customs services at airports and harbours.

The following aspects will be discussed: (1) Potentiometric study of the affinity of aptamers for cocaine and its cutting agents by comparing several cocaine binding aptamers one to another and to random aptamer sequences of the same length ; (2) electrochemistry of cocaine and cutting agents to discover their redox processes and increase our understanding about isolating the electrochemical response of cocaine ; (3) electrochemical study of powder samples by swiping screen printed graphite electrodes over the samples and using gelatin hydrogels as solid electrolytes; (4) immobilization of aptamers in gelatin matrix.

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CYCLIC VOLTAMMETRIC STUDIES ON SOME HUMAN METHAEMOGLOBIN PHENOTYPES AND APPLICATIONS IN THE IDENTIFICATION OF THESE PHENOTYPES

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The iron atom in the haemoglobin(Hb) molecule is responsible for some notable physiological functions of the molecule. Chen et al., [1] reported concentration- dependent values of peak current in the cyclic voltammetric (CV) studies of bovine Hb using bare glassy carbon electrode. Ogunlesi et al.,[2] using similar electrode system reported that values of the peak current at -220mV could be used for the determination of human Hb phenotypes. In this report CV studies were carried out on methaemoglobins A, S, AS, AC and F in 0.2 M phosphate buffer pH 6.2 using platinum as working electrode, platinum wire as auxiliary and silver/ silver chloride as reference. The potential window was 600mV, initial and final and zero as switching potential. The iron atom in metHb as well as in ferricyanide ion exists in an octahedral complex and thus in these studies potassium ferricyanide was used as reference. The reduction and oxidation peak voltages for 2mM ferricyanide were 224-229mV and 294-295 mV respectively. The corresponding values for similar concentrations of metHbAC were 189mV and 273 mV while the values for metHbAS were 172mV and 275mV. The value of the reduction peak voltage appears to be characteristic of the Hb phenotype. Correlations between the values of the peak current and Hb concentrations and between the relative values of peak current and the Hb phenotypes were also investigated.

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TIME RESOLVED IMPEDANCE SPECTROSCOPY OF A REDOX POLYMER FOR DETECTION OF ENZYMATIC PROCESSES

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pH-responsive redox polymers have been in the last decades drawing interest due to their electron transfer rate dependent on pH [1]. This is due to the change of their swelling properties regulated by different pH values. Over the years many systems were developed, leading finally to detection of non-redox events which affects the polymer properties [2,3]. Electrochemical impedance spectroscopy is a powerful tool to determine the electrochemical reaction rates. However, it requires stable conditions and cannot be used to directly address systems which change dynamically, such as enzymatic processes. In our study, a hydrolase enzyme like urease, which is evoking a pH change by converting urea to ammonia, was embedded in an Osmium modified poly (vinyl) imidazole. Despite its stability during cyclic voltammetry measurements, it degrades too rapidly upon polarization above its formal potential to measure reliable impedance spectra. To overcome this issue the impedance was studied dynamically superimposing a multisine to the cyclic voltammetry. The polymer resulted stable for hours, without showing any appreciable decrease in performances. Moreover, the true time resolved impedance can be studied as function of potential or time, opening to more sophisticated experiments: such as the injection of urea which causes a local change of pH in the polymer. Besides the application to our case, the time resolved impedance spectroscopy, which visualizes the changing in the impedance in real time, opens to a new way to investigate many other systems which are evolving during time.

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COMMERCIAL MESOPOROUS TITANIUM DIOXIDE AS A SUPPORT FOR HORSERADISH PEROXIDASE FOR BIOELECTROCHEMICAL APPLICATIONS

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Porous materials are finding important applications in the fields of science and technology as adsorbents, supports for catalysis and (bio)sensors. According to the IUPAC definition, porous materials can be divided into three classes: microporous (pore size <2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) materials [1].

Because of their large surface and uniform pore size distribution in the same dimensions as biomolecules, mesoporous materials have been immobilized on electrodes and impregnated with biomolecules to form biosensors [2]. Horseradish peroxidase (HRP) contains redox active center in its catalytic site. It is commonly used as a label in immunoassays and as a redox active enzyme in biosensors, which are particularly designed for detection of H2O2, phenols and its derivatives [3].

In this work, for the first time, we suggest using commercial mesoporous TiO2 as a matrix impregnated with a model redox enzyme HRP, with the aid of a mediator to detect hydrogen peroxide (H2O2) by amperometry. The immobilization strategy and the electrocatalytic behaviour towards H2O2 will be discussed. A generic platform for sensing applications, in which commercial mesoporous titania is used as a support for biomolecules, is proposed.

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BIOELECTROCHEMISTRY IN MOLECULAR ONCOLOGY

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Electrochemical (EC) analysis is an interesting alternative to currently employed methods in biomedicine, based predominantly on optical detection, especially due to its low cost and simple instrumentation. Moreover, it provides an automatic, parallel detection of multiple samples using miniaturized electrode chips [1]. Here, we show our recent results using EC analysis to study various topics in cancer research, including (a) detection of specific microRNA sequences [2-4], which play role in carcinogenesis as potential biomarkers, (b) study of DNA methylation, an important epigenetic modification [5], or determination of ferrocene-based derivatives as promising antitumor drugs inside human cancer cell lines [6]. Electrochemistry could thus be a simple and inexpensive tool in current molecular oncology, especially for rapid screening or for complementing existing methods. Authors wish to thank GACR 14-24931P.

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APPLICATION OF NANOMATERIALS COMPOSITE MODIFIED ELECTRODES FOR GLUCOSE BIOSENSORS, BIOFUEL CELLS AND ELECTROCHEMICAL DETERMINATION OF BIOMOLECULES

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We prepared various carbon based composite materials (graphene and Multiwalled carbon nanotube) for the successful immobilization of glucose oxidase (GOx) and the resulting modified electrodes have been used for the assembling of glucose/O2 biofuel cells. Multiwalled walled carbon nanotubes (MWCNT) have large surface area, high electrical conductivity, promising chemical and thermal stability. Similarly graphene, a two dimensional allotrope of carbon also possess excellent physicochemical properties. Nevertheless, nanocomposites of electrochemically reduced graphene oxide (ERGO) – MWCNT could collectively harvest all the above promising properties of the two carbon allotropes. We constructed a simple membraneless glucose/O2 biofuel cell by assembling MWNTs/GOx modified electrode as the anode and Pt electrode as the cathode and achieved the maximum power density of 65 µW/cm2 with an open circuit voltage (Voc) of 0.58V. Afterwards we assembled ERGO/GOx biocomposite as the anode compartment and MWCNT/ZnO/laccase modified electrode as the cathode compartment and achieved the power density of 54 nW/cm2 with Voc of 0.055V. We also used ERGO-MWCNT modified glassy carbon electrode (GCE) as anode and graphene-Pt composite modified GCE as cathode and harvest the maximum power density of 46 µW/cm2 with Voc of 0.4V. We have developed a novel biocomposite material for the electrocatalysis of p-acetamidophenol using Multi-walled carbon nanotubes (MWCNTs) and poly (aniline) and poly (flavin adenine dinucleotide) copolymer (PANIFAD) at gold electrode and screen printed carbon electrodes (SPCE). The developed MWCNTs-PANIFAD biocomposite film for the electrocatalysis combines the advantages of ease of fabrication, high reproducibility and sufficient long-term stability. In another approach we have fabricated metal hexacyanoferrates-conducting polymer film based sensor for the simultaneous determination of p-acetamidophenol and ascorbic acid.

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BREATHING THROUGH A WIRE: ELECTRO-ENZYMOLOGY OF Q-WIRED RESPIRATORY COMPLEXES

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Because of their highly conjugated nature, oligo(phenylenevinylene)s (OPVs) can be considered to be 'molecular wires' [1]. When attached to a redox center on one side and an electrode anchoring functionality on the other, redox-active self-assembled monolayers (SAMs) can be prepared on an electrode surface. In addition to enabling fast (non-rate limiting) electron transfer from the electrode to the redox center, these OPV tethers may ensure proper orientation of the redox center relative to the electrode surface [2, 3].

Here, we introduce novel, bifunctional OPV molecular wires equipped with a gold binding methyl thiol anchor group on one side and a ubiquinone head group on the other. Because the ubiquinone group retains its natural redox properties and ability to bind to enzymes that use ubiquinone as natural substrate, SAMs of these wires provide a better defined electron pathway between electrode and enzyme. These 'Q-wires' may ultimately aid in enzyme immobilization, enabling the investigation of the enzyme's redox properties using Protein Film Voltammetry (PFV), a versatile technique for studying the electrochemistry of surface-confined redox enzymes.

A brief overview of the synthesis of the 'Q-wires' will be presented, along with their electro-chemical properties and their interactions with different quinol oxidizing enzymes, such as, for example, cytochrome bo3, which functions as the terminal oxidase in the respiratory chain in aerobically grown E. coli cells.

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CHARACTERIZATION OF BIOLOGICAL SYSTEMS AND SEMICONDUCTOR MATERIALS FOR ENERGY CONVERSION DEVICES BY MEANS OF SCANNING PHOTOELECTROCHEMICAL MICROSCOPY

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The biological photosystems are highly abundant natural protein complexes involved in the photosynthetic process. They act as photodiodes exciting electrons across the thylakoid membrane upon absorption of visible light. Taking advantage of the high yield of these biomolecules in light collection, the photosystems can be used in the development of highly efficient biophotovoltaic devices. On the other hand, many new photoelectrocatalytic materials based on ternary and quaternary metal oxides have been developed in recent years for their use as photoelectrodes for solar water splitting, showing promising properties still to be improved regarding their limitation by slow water oxidation kinetics and poor charge separation. The study and characterization of both, inorganic and biological systems, will allow the development of efficient state-of-the-art devices for solar-to-chemical energy conversion.

We present the use of Scanning Photoelectrochemical Microscopy (SPECM) as a tool for the local assessment of photoelectrochemical processes at the micro scale. SPECM was developed as a new device for the evaluation of electrochemical pro-cesses occurring at substrates modified with biomolecules or at the semiconductor-electrolyte interface, allowing a localized illumination of the analysed sample and a high resolution analysis of evolved molecular oxygen or hydrogen. Examples including the analysis of semiconductor materials as well as biological photo-systems will be shown.

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BIO-ELECTROCHEMISTRY: MICRO/NANOSCALES

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FILMS AND SUSPENSIONS CONSISTING AU AND PT NANOPARTICLES FOR CATALYTIC ELECTROOXIDATION OF GLUCOSE

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Electrodes modified with oppositely charged Pt and Au nanoparticles exhibit electrocatalytic synergy of glucose oxidation in alkaline solution. Such a simple method of preparation of bimetallic nanoparticulate films produces an electrode with significant shift of the onset potential and larger current density as compared to electrodes prepared only from platinum or gold nanoparticles. The observed effect results from close proximity of the Au and Pt nanoparticles surfaces within the film. No alloying was detected by X-ray photoelectron spectroscopy or X-ray diffraction measurements. The electrocatalytic synergy was also observed in experiments with glassy carbon rotating disc electrode in bimetallic suspension prepared from Pt and Au nanoparticles having the same charge. On the basis of X-ray photoelectron spectroscopy and cyclic voltammetry experiments it was concluded that electrocatalysis occurs on nanoparticles adsorbed during experiment from suspension on glassy carbon electrode

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CARBON NANOPARTICLES @ MOS2 NANOFLAKES AS A NEW HYBRID MATERIALS FOR ELECTROCATALYTIC OXIDATION OF BIOLOGICALLY ACTIVE COMPOUNDS

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Electrodes modified with MoS2 nanoflakes decorated with functionalised carbon nanoparticles allows for separation of the voltammetric signal of dopamine from the signals of interferences. The decoration process was conducted in sonicated suspension of both components. The glassy carbon disc electrodes were modified by drop casting of hybrid material suspension. Scanning electron microscopy reveals that MoS2 nanoflakes stacks are covered by carbon nanoparticles. The hybrid films were also characterised by X-ray photoelectron spectroscopy and Fourier transformed infrared spectroscopy. Cyclic voltammetry reveals an increase of electrochemically active surface upon modification. The studied hybrid materials exhibits electrocatalytic properties towards epinephrine and dopamine oxidation and allows for separation of voltammetric signal of the latter from that of ascorbic and uric acid.

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SCANNING ELECTROCHEMICAL MICROSCOPY OF ALIVE, FIXED AND PERMEABILIZED MELANOMA CELLS

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Scanning electrochemical microscopy (SECM) is a surface reactivity characterization technique based on an electrochemical signal record at a probe positioned or scanned in close proximity to a substrate. SECM has demonstrated to be a useful tool for the electrochemical imaging and intracellular investigation of living cells. However, the interpretation of the experimental data obtained from living cells can be difficult due to i) cell to cell variability in terms of metabolic activities, ii) possible dynamic morphological changes of cells and iii) experimental time restrictions. Alternatively, working with fixed cells (e.g. treated with paraformaldehyde and/or methanol) leads to the elimination of biological activity of cells, but opens the opportunity to access more easily the preserved cellular ultrastructure as well as cells proteins. The paraformaldehyde fixation can be used for SECM to investigate the topography or the passive transport of the redox mediator through the membrane in a constant height scanning mode while the methanol fixation can open the intracellular compartment to be analysed by SECM.

In this contribution, different melanoma cell lines representing progressive stages of skin cancer development were studied by SECM in the feedback mode. The data were collected for living cells, cells fixed with formaldehyde and cells fixed with methanol. Depending on the employed cell fixation procedure cells were able to provide both positive and negative feedback by using the same redox mediator based on the ability of the redox mediator to access the intracellular space and to react with electrochemical active species (e.g. proteins). For a better understanding the nature of the feedback signal, the influence of the redox mediator type (charged or non-charged), the ultramicroelectrode size and the probe translation speed were investigated. Additionally, SECM images of protein spots on a PVDF membrane were performed.

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ELECTROCHEMICAL IMMUNOSENSOR WITH NANOELECTRODES ENSEMBLE FOR DETERMINATION OF IGY: IDENTIFICATION OF EGG-YOLK AS BINDER IN TEMPERA PAINTINGS

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This work presents a nanostructured electrochemical immunosensor suitable for detecting proteins of interest in cultural heritage conservation, in particular in tempera paintings. We focus here on the determination of immunoglobulin IgY as a marker of the presence of hen egg yolk egg yolk used as paint binder. The chosen transducers are Nanoelectrode Ensembles (NEEs), prepared by template electroless deposition of gold in track-etched polycarbonate membranes. Because of their geometry and diffusion behaviour, NEEs are characterized by significantly low detection limits; moreover they display the capability of capturing proteins by interaction with the polycarbonate membrane of the NEEs. Firstly, the protein component of the paint sample is extracted by sonication in phosphate buffer, then IgY is captured on the polycarbonate surface by incubation on the NEE. The immunoglobulin is detected by treatment with anti-IgY antibody labelled with horseradish peroxidase (Anti-IgY-HRP). In the presence of hydrogen peroxide and methylene blue, the binding of the Anti-IgY-HRP generates an electrocatalytic signal useful for the determination. The capability of the sensor to detect egg yolk in paintings was tested by analysing both paint models, prepared in the lab, and real samples, from paintings of the XVIII–XX century. Multivariate exploratory analysis was applied to classify the voltammetric patterns; the results confirm that the electrochemical nano-immunosensor furnishes selective responses and is able to differentiate egg-yolk tempera from other kind of tempera binders as well as from acrylic or oil paints.

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METAL-ORGANIC FRAMEWORK/ZINC OXIDE HYBRID MATERIAL SYNTHESIS USING FAST AND SIMPLE METHOD

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Metal-organic frameworks (MOFs) are crystalline, solid materials consisting of metal ions or clusters bound via coordination bonds to organic linkers. Remarkably porous and fascinatingly tuneable, MOFs have found use in fields such as catalysis, sensing and drug delivery. [1] Combining MOFs with other functional materials allows for the formation of hybrids, containing the unique properties of its components. Here, we investigate the formation of a hybrid material combining ZIF-8 and zinc oxide. Remarkable stability and ease of synthesis have made ZIF-8 one of the most well-known MOFs, with applications in biosensing and catalysis. [2] Yet, ZIF-8 thin film formation remains a challenge, often requiring harsh conditions, multiple synthesis steps and long synthesis times. [3] Zinc oxide is a biocompatible semiconductor with high electron mobility, possessing a large variety of morphologies. This has led to its investigation alongside many materials, including enzymes for biosensing. [4] Yet its use alongside MOFs has been relatively unexplored. Here, we utilize zinc oxide as zinc ion source and nucleation site for the formation of ZIF-8 thin films. This is achieved by simply depositing a small amount of organic linker solution onto electrochemically grown zinc oxide nanorods. Solvent evaporation leaves a thin film of linker coating the zinc oxide nanostructures. The ZIF-8 thin film is formed upon heating, while zinc oxide nanorod morphology is maintained, yielding a nanostructured hybrid thin film. This method is fast and simple, requiring less than an hour and only an oven. The hybrid thin film can be used for biosensing.

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POSTER PRESENTATIONS

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NANOSCALE ELECTROCATALYSIS AND IN SITU SCANNING TUNNELING MICROSCOPY OF HUMAN SULFITE OXIDASE ON SINGLE-CRYSTAL AU(111) ELECTRODE SURFACES

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Human sulphite oxidase (hSO) is a redox metalloenzyme central in the biological sulphur cycle where it catalyses the conversion of sulphite to sulphate. The enzyme holds a molybdenum- and a heme-domain and is of interest due to its potential in areas of biosensors and other bio-electronics. We have studied the electrocatalytic properties of hSO immobilized on Au-electrode surfaces. A novel approach is that the enzyme is immobilized on single-crystal atomically planar Au(111) electrode surfaces via a variety of self-assembled monolayers (SAMs) of differently functionalized thiols. Cyclic voltammetry and in situ scanning tunnelling microscopy (in situ STM), resolved to the level of the single enzyme molecule have been employed to investigate electrocatalysis of hSO at the nano scale.

Using sodium acetate as a supporting buffer electrolyte gave the most promising result for both electrochemistry and in situ STM. SAMs of L-cysteine and aminothiols of carbon chain lengths of 2, 6, 8, 11, and 16 carbon atoms were used as linkers to immobilize hSO on Au(111). Using L-cysteine gave no catalytic current. By increasing the aminothiol chain length, the catalytic current first increased up to 8 carbon atoms and then followed by current decrease, suggesting an optimal chain length of around 8 carbon atoms. A ratio of 3:1 9-mercapto-1-nonanol and 6-amino-1-hexanethiol showed stronger catalytic activity, but smaller catalytic currents, suggesting lower surface coverage but with better enzyme orientation for electrocatalysis. Observations by the first in situ STM imaging of hSO in electrocatalytic action to single-molecule resolution indicate a low surface coverage of hSO on the single-crystal Au(111) surfaces. In situ scanning tunnelling spectroscopy discloses further a pronounced dependence of the single-molecule electrocatalytic current on the electrochemical overpotential that approaches a molecular scale view of electrochemical enzyme kinetics.

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EFFECT OF NANOPARTICLES ON THE EFFICIENCY OF APTASENSORS: A COMPARATIVE STUDY AND THE APTAMER OF E. COLI AS A MODEL

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An electrochemical aptasensor based on carbon paste electrode (CPE) modified with different nanoparticles such as gold nanoparticles (Au), silver nanoparticles (Ag), hollow gold nanosphere (HGN), hollow silver nanosphere (HSN), silver-gold core:shell (Ag@Au), gold-silver core:shell (Au@Ag) and silver-gold alloy nanoparticles (Ag/Au) was developed. The main goal of this project was qualitative investigation of nanoparticles with different structures on the efficiency of aptasensor. No detailed information is available in the literature on the comparison between nanoparticles in aptasensing. Here, the aptamer for Escherichia coli (E.coli) bacteria was selected as a model. To prepare the modified CPE, the cysteamine was bound onto the surface of CPE by using cyclic voltammetry. Then, nanoparticles were self-assembled on the electrode via strong covalent bond to fabricate the nanoparticles self-assembled modified electrode. The morphology of the modified electrode was characterized with scanning electron microscopy. The electrochemical behaviour of E.coli on the bare and modified CPE was investigated with cyclic voltammetry and differential pulse voltammetry in a 0.1 M pH 6.0 phosphate buffer solution. Two well-defined oxidation peaks of E.coli on the bare CPE were obtained at + 0.81 V and + 0.95 V (vs. Ag/AgCl) that can be attributed to the oxidation of guanine. While after aptamer immobilization at the nanoparticle modified CPE, one peak appeared at + 0.95 V (vs. Ag/AgCl) that probably belongs to the synergic effects of nanoparticles and aptamer. The peak current of E.coli was linear with its concentration in the range of 1.0 to 10+6 CFU. To obtain optimized condition, further studies were done by Apt/Au/Cys/CPE including effect of different modified layer on nanoparticles adsorption, aptamer immobilization as well as selectivity of the aptasensor using other kinds of bacteria.

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CARBON FUNCTIONALIZED PAPER BASED SENSORS

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Paper based disposable sensors are very promising for biomedical analysis where fast, cheap and easy to use tools are requested. New stochastic sensors based on carbon thin films deposited on adsorbent and glossy papers modified with nanostructured material such as 5,10,15,20-tetraphenyl-21H,23H-porphyrin were development and used to detect carcinoembryonic antigen (CEA), a biomarker very often used for cancer diagnosis as well as for follow up of cancer treatment. Qualitative and quantitative assay of CEA from whole blood samples was performed using the new proposed sensors. The sensors can be used as disposable sensors for biomedical analysis with high sensibility (5.34x 105 s mg/mL) and lowest limit of determination (160 ng/mL).

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A CHEMOMETRIC APPROACH FOR OPTIMIZING AN AMPEROMETRIC IMMUNOASSAY ON A SCREEN PRINTED ELECTRODE FOR CLOSTRIDIUM TETANI ANTIBODY DETERMINATION IN SERUM

Stéphanie Patris, Marie Vandeput, Gersonie Momo Kenfack, Dominique Mertens, Bieke Dejaegher, Jean-Michel Kauffmann

An immunoassay for the determination of anti-Clostridium tetani antibodies, using a screen-printed electrode (SPE) as solid support for antigen immobilization, has been developed. The immunoreaction and the subsequent amperometric detection occurred directly onto the SPE surface. The assay consisted of spiking the sample directly onto the toxoid modified SPE, and then a HRP-labelled anti-IgG, was added. Amperometric detection was realized by spiking a solution of hydroquinone directly onto the SPE.

A chemometric approach was implemented for the optimization of the immunoassay. The variables of interest such as BSA concentration, incubation times and labelled antibody concentration were varied with the aid of the response surface methodology using a central composite design. The latter permitted to investigate the combined effects of the variables and allowed to find the optimal experimental conditions of the parameters in a minimum of experiments. Since 4 experimental parameters were studied, a minimum of 25 experiments had to be conducted: 2 exp. 4 + 2 x 4 + 1 (center point). The experimental design was carried out in seven days and the center point was repeated once daily (7 times) to evaluate the variability of the model. Five test points were added to validate the constructed model. A total of 36 experiments were necessary for the entire study.

It was observed that 2 factors had the greatest impact on the response: the first incubation time and the dilution of the HRP-anti-IgG. To maximize the response, the dilution should be small, while the first incubation time, i.e. the anti-tetani antibody incubation, should be long. The BSA concentration and the second incubation time, i.e. the HRP-anti-IgG incubation, had very limited influence. With the optimized conditions, the immunoassay has a limit of detection of 0.011 IU/mL and a limit of quantification of 0.012 IU/mL. These values are beneath the protective antibody limit of 0.06 IU/mL established by an ELISA.

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ELECTROCHEMICAL AND SPECTROSCOPIC INVESTIGATION OF CU(II) AND NI(II) COORDINATION TO THE DESIGNED ATCUN PEPTIDES

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Due to the diversity of functions performed in living organisms, proteins are extremely important and interesting subject of research. One of the determinants of the biochemical activity of proteins or smaller peptide structures is their ability to coordinate selected metal cations. Complexes which are formed through these specific interactions can have a positive or negative influence on people's health. It is worth noting that in some cases the properties of a whole protein are determined by its small fragment. Thus, obtaining a possibly complete characterization of this piece can be a key to understanding many processes of biological importance.

The purpose of this study was to investigate the coordination properties of selected oligopeptides having the following amino acid sequence: Xxx-Xxx-His, where Xxx stands for any amino acid, His stands for histidine. Tripeptides which in the third position (C-terminus) imply histidine are called ATCUN peptides. A strong affinity for Cu(II) and Ni(II) cations is what makes them unique among other tripeptides. In this context the electrochemical properties of such complexes seem to be particularly interesting for us.

Various voltammetric methods were used in this work to acquire valuable information about kinetics and thermodynamics of the formation of oligopeptide complexes. In addition, spectroscopic measurements (UV-Vis spectroscopy) were carried out to complement the obtained results. Exploring the impact of amino acid sequence on the coordination abilities of selected ATCUN peptides not only provides a better understanding of coordination process but it may also become an introduction to more advanced researches which assume selective hydrolysis powered by peptide-Cu/Ni(II) complex formation and electrochemical metal oxidation.

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ASSESSMENT OF ENZYME INHIBITORS IN A FLOW SYSTEM WITH ELECTROCHEMICAL DETECTION

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The identification of inhibitors that modulate enzyme activity is an ongoing research in pharmaceutical industries due to their large applications in the medical area. Indeed, inhibitors have emerged as an important class of drugs to treat human diseases. They are also used in agriculture as pesticides.

In order to screen and assess new inhibitors, an original method was developed by flow injection analysis with a biodetector consisting of an immobilized enzyme and an electrochemical detector. The thin-layer flow-through amperometric detector was customized in an original design with: upstream, a gold disk support for the enzyme immobilization and downstream, a working disk electrode for the enzymatic product detection.

This original analytical tool was applied to investigate inhibitors of two well-known enzymatic systems i.e. acetylcholinesterase inhibitors using a silver working electrode and tyrosinase inhibitors using a glassy carbon working electrode. The on-lines studies were realized in phosphate buffer and the optimal conditions for incubation time, applied potential, pH and flow rate were established.

The developed setup permitted to study both the inhibitor potency and the recovery rate of the enzyme for the different inhibitor drug compounds studied. This method is characterized by its relative low cost, enzyme stability and reusability and it represents a useful innovative approach for fast screening of potential drug inhibitors.

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ELECTROCHEMICAL PROPERTIES OF COPPER COMPLEXES WITH NATRIURETIC PEPTIDES

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The heart arterial muscle produces and secretes atrial natriuretic peptides/factor (ANF). ANF peptide is associated with several biological effects such as natriuresis, hypotension, but also an inhibitory effect on renin and aldosterone secretion is observed. Biological studies indicated that a disulphide-looped sequence of 17 amino acids plus COOH-tail containing NSFRY sequence induce the biological activity of ANF (28-peptide).

The NSFRY peptide is expected to coordinate effectively metal ions such as Cu(II) and Ni(II). Although NSFRY has non-coordinating side chains its complexes with copper ions are extremely stable. The affinity of NSFRY toward Cu(II) ions was investigated by potentiometric, calorimetric and spectroscopic methods. However, as far as we know, no voltammetric studies have been conducted till now.

The main goal of this work was to investigate the interactions between copper(II) ions and NSFRY peptide. Voltammetric studies were performed to determine the structure of Cu(II) complexes of a group of NSFRY-NH2 peptides analogues. The influence of peptide sequence as well as pH dependent coordination structure of ANF-Cu(II) complexes on their redox properties was studied. The proposed approach could provide better description of the ANF-Cu(II) complex formation and thus could be helpful in the understanding of the pathogenesis of the heart failure. Presented results are promising for the elucidation of the relationship between structural and redox properties of active copper centers not only in NSFRY-Cu(II) complexes but also, in different copper dependent proteins.

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FABRICATION AND OPTIMIZATION OF SERS SUBSTRATES FOR DNA HYBRIDIZATION DETECTION BY MEANS OF WIRELESS ELECTROCHEMISTRY

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Surface enhanced Raman spectroscopy (SERS) is a powerful analytical tool for fingerprint analysis and single molecule detection. SERS substrates exhibiting a high surface roughness are important for substantially enhancing the signal intensity. In addition, nanostructures which are used to generate localized plasmons (hot spots) on the sample surface contribute to the enhancement of the signal intensity. Various electrochemical techniques have been used to fabricate such nanostructured or highly rough SERS substrates. In this study, we employed bipolar electrochemistry (BPE) as a tool for the preparation of nanostructured SERS substrates based on inverse opal structures.

We present a fast and effective approach to prepare and optimize nanovoid modified SERS substrates. First, polystyrene nanobeads with a diameter of 300 nm were deposited on a smooth gold wafer via the Langmuir-Blodgett technique. Subsequently, a gold layer was deposited on the beads-modified wafer using BPE. The amount of deposited gold is proportional to the gradually changing potential along the electrode surface. Thus, the control of the thickness of the gold layer could be well adjusted to form nanovoids with different dimensions upon removal of the polystyrene beads by dissolution in dichloromethane. To estimate the optimal nanovoid size with respect to high signal intensities in the SER spectra, the correlation between nanovoid size and peak intensity was monitored using para-nitrothiophenol (p-NTP) as Raman active molecule. Based on these results the optimal surfaces were used for the detection of DNA hybridization. A dsDNA specific intercalator, i.e. proflavine, which is Raman active, was employed for the detection of the DNA hybridization process.

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TEMPORAL RELATIONSHIP BETWEEN SYNAPTIC ACTIVITY AND AB GENERATION IN VIVO

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Alzheimer's disease (AD) is initiated by the progressive accumulation of amyloid-β (Aβ) peptide in the brain as toxic structures such as Aβ oligomers and plaques. In vivo imaging studies in humans show that plaques are found in regions of the brain that display high levels of neuronal activity, sometimes referred to as the default mode network. Direct modulation of synaptic activity dynamically regulates brain Aβ levels in awake animals with increased synaptic activity increases brain interstitial fluid (ISF) Aβ levels and vice versa for suppressed activity. These findings strongly suggest a close temporal relationship between synaptic activity and Aβ generation. We have previously used an in vivo microdialysis technique to measure dynamic changes in Aβ levels in the mouse brain every 30-60 minutes. However, Aβ generation likely occurs on the order of seconds to minutes. We have recently adapted an electrochemical technique to study Aβ in vivo on a much faster time scale. The principle behind this approach is that Aβ contains an electroactive tyrosine amino acid at position 10. A voltage applied to the electrode induces oxidation of the tyrosine residue, which releases electrons that the carbon fiber detects as electrical current. We have covalently attached anti-Aβ antibodies to the electrode surface to provide specificity for Aβ detection to the exclusion of the other proteins and molecules present within the brain extracellular space. In our published studies (Prabhulkar et al., 2012) we show that MIEs containing anti-Aβ antibodies can specifically detect either Aβ40 or Aβ42. In vivo MIE studies show that we can very rapidly, within a minute, detect brain ISF Aβ levels in APP transgenic mice, allowing us to assess fast-acting mechanisms that directly regulate ISF Aβ. Using MIEs in vivo, we are able to detect a rapid increase in ISF Aβ following a rise in synaptic activity. Micro-immunoelectrodes provide a novel way to explore mechanisms of this relationship.