Book of Abstracts

SMCBS'2009 International Workshop

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20:00 Poster 01

Highly effective and sensitive sensor based on thin ordered protein layers

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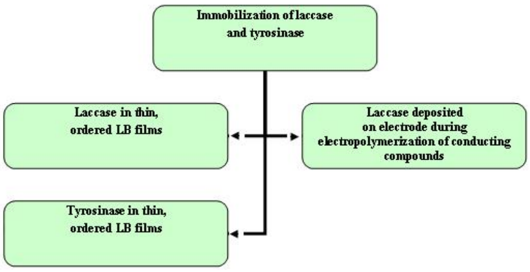
Physical entrapment within conducting material matrix is the widely used procedure of enzyme immobilization for sensor application due to its simplicity, uniform distribution of biomolecules within the film and applicability to a various proteins. To optimize the enzyme deposition and the layer stability several methods are developed including use of amphiphilic monomers or employing affinity interactions between biomolecules and polymers substituted with appropriate bio-compatible groups [1].

Several methods for protein architecture are reported i.e.: layer-by-layer technique, electrodeposition and Langmuir-Blodgett (LB) technique.

LB technology is known as a useful method for the formation of well-oriented film of bio/organic material on a solid substrate, because it can control the degree of order and packing density of protein and especially minimize the loss of protein activity [2]. The structures and moieties of this type of layers with embedded immobilized enzymes are of great interest because of their biosensor applications.

Another common method for immobilization enzymes is electropolymerization and electrodeposition. Electropolymerization methods have been extensively used to create immobilized enzyme electrodes with conducting polymers. The polymer forms a self-assembled monolayer by electrostatically adsorbing to a charged surface.

Continuing systematic investigation in fabrication of protein – conducting material sensitive layers [3], we reported here the results of research directed into the properties of laccase from *Cerrena unicolor* and tyrosinase from *Agaricus bisporus* integrated to thin films (LB films, electropolymer layers, *Scheme*). The immobilized phenoloxidases proved to be an excellent as a bioanalytical tool for monitoring phenolic pollutants. Furthermore, the sensor sensitization can be achieved by interlacing to ordered film conducting amphiphile according successful previous experience (ie carbazole and diphenylamine derivatives) [4]. Conducting polymer - poly[(*N*-nonylphenoxazine-3,7-diyl-*alt*-(1,2,3-benzothiadiazole)] admixed into the film is supposed to be a good mediator element in phenol oxidases sensor. The interlaced polymer is expected to facilitate the electron transfer as well enhancing the sensor sensitivity.



Scheme. Immobilization methods of phenoloxidases

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20:00 Poster 02

Anaerobic digestion monitoring - application of flow-through sensor array

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Electronic tongues (ETs) based on potentiometric sensor arrays are often used for fast, inexpensive and reliable foodstuff classification, origin recognition, estimation of complex samples' properties, etc. In the last few years they were also applied for various fermentation monitoring (eg. Aspergillus niger fermentation, batch Escherichia coli fermentation, etc.), as a devices capable of automated and online control of the process . In this work a novel application for ET is proposed – miniaturized flow-through sensor array was used for classification of samples obtained during anaerobic digestion of whey in bioreactor working in periodic conditions.

Potentiometric sensor array composed of ion-selective electrodes (ISEs) was applied to estimate fermentation stage and stability of the anaerobic digestion process. Flow through cell was constructed on the basis of single modules to be connected with each other, in which miniaturized ISEs were mounted. The array was composed with the use of sensor sensitive towards acetate anions, lipophilic anions, lipophilic cations, amines, and some simple ions (H+, NH4+, Na+). Samples were gathered from three batches of fermentation running for seven days.

The objective was to determine Volatile Fatty Acid (VFA) level and Chemical Oxygen Demand (COD) of samples by means of sensor array outputs processed by Partial Least Squares Analysis (PLS). The results of COD determination are presented in Figure 1. It was found, that the predicted values of both VFA level and COD were in good accordance to the real ones.

The preliminary results show, that potentiometric ET can be applied to anaerobic digestion monitoring, and detailed studies will be a subject of our future work.

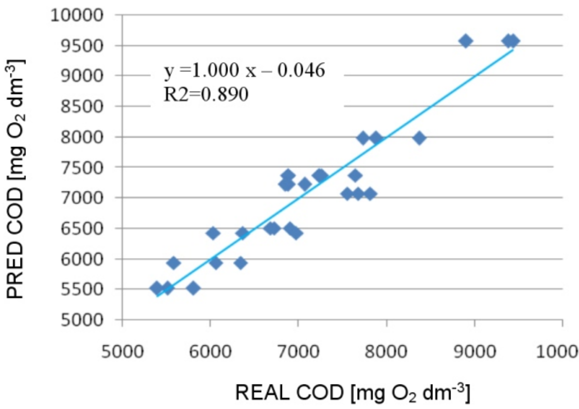

Figure 1. Results of COD determination

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20:00 Poster 03

Preparation of copper hexacyanoferrate multilayer films modified with 4-(Pyrrole-1-yl) benzoic acid on glassy carbon electrode.

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During the last years nanostructured films were used for electrode modifications. The hybrid inorganic-organic multilayers films were obtained based on the interaction of the film components. The layer-by-layer (LBL) method was very often used for fabrication of such nanostructured films. Hybrid nanostructured organic, and inorganic-organic films produced by LBL technique can be used for investigation of new approach in electrochromism, electrocatalysis, bioelectrochemistry and electroanalysis. Much attention has been paid also to the metal hexacyanoferrates used as redox mediators in LBL-type films since they are mixed valency clusters exhibiting relatively fast electrons transfer in reduction and oxidation processes [1]. The layer-by-layer method was used for preparation of multilayer hybrid conducting polymer stabilized copper hexacyanoferrate films in which 4-(pyrrole-1-yl) benzoic acid (PyBA) grafted on the glassy carbon electrode (GC) was exposed to Cu^{2+} and $[Fe(CN)_6]^{3-}$ solutions. It is known [2] that 4-(pyrrole-1-yl) benzoic acid forms monolayers on GC electrode. The surface pKA of 4-(pyrrole-1-yl) benzoic acid adsorbed layer was estimated from cyclic voltammetric measurements of electron transfer processes of $[Fe(CN)_6]^{3-/4-}$ in the solutions of various pH's. The copper hexacyanoferrate-PyBA multilayer films exhibited well-defined electrochemical behavior and high stability. Electrode reactions of such films were found to be sensitive on the presence of various alkali metal, NH4$^+$ or Tl$^+$, ions. The selectivity coefficients , $K_{K/M}$, of such composite electrode were estimated. One should also stress that observed voltammetric peaks for the studied system have been well-defined and well-separated from other electrode reactions what makes such electrode useful in potential applications.

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20:00 Poster 04

Ion transfer across the liquid|liquid interface studied with membrane-modified screen-printed electrodes

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The interface between two immiscible liquids attracts the attention as for fundamental studies as for possible applications. Thus it can be considered as a model of a half of living cell membrane. That is why particles transfer processes, including ion transfer, across the interface have a fundamental importance in nature and in case of sensor systems development.

The main goal of present work was to research ion transfer across the interface between two liquids.

Screen-printed electrodes modified by membranes of polyvinylchloride plasticized by water-immiscible organic solvent was utilized as a disposable electrode setup with the interface between two immiscible liquids. Hydrophobic redox probe (erbium bis(tetra*tert*-butylphthalocyaninato)) was inside membrane phase. The redox pro-

cess was accompanied with the ion transfer across liquid-liquid interface. The formal potential of observed redox activity depended on nature of background electrolyte: more hydrophobic ions transfer on more less potentials that more hydrophilic ones. In present work dependence of ion transfer from nature and concentration of background electrolyte were studies. It was shown that increasing of ions concentration promotes decreasing of transfer energy.
This electrode system was used for biomolecules registration.

20:00 Poster 05

Synthesis and application of library of artificial receptors immobilized on cellulose support

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We found that supramolecular structures formed by self-organisation of monolayer of
N-lipidated peptides attached to the CH$_2$OH groups of cellulose support via aminophenylamino-1,3,5-triazine are able to create ”holes” and “pockets” in dynamic equilibrium, which can very efficiently recognized the structure (shape, size and polarity) of small guests molecules [1]. The supramolecular structures formed from *N*-lipidated peptide chains are highly flexible, therefore it has to be expected, that the host adjust its shape to fit the guest molecule most efficiently, resembling natural receptors. The array of the artificial receptors have been synthesized and used in the studies. Thus, even in the case, when the single receptor in a differential array does not necessarily have selectivity for a particular analyte, the combined fingerprint response can be extracted as a diagnostic pattern visually, or using any chemometric tools [2]. The selectivity of binding was studied by experiments involving triphenylmethyl dyes. It has been found that any changes of size, polarity, hydrogen bonding ability of substituents of phenyl groups altered the binding profile. Based on this observation, we concluded that the selectivity of binding depends on the structure of peptide and lipidic fragment of the artificial receptor and vary with the analyte structure. An attempts were made to rationalise the relation between binding pattern and structure of receptor and analyte using SAR studies.

Acknowledgements: The study was supported by the Ministry of Science and High Education under the Research Project N N204 326737.

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20:00 Poster 06

Oxidation of glucose at nanostructured composite bioelectrocatalytic systems

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We propose new bioelectrocatalytic system containing carbon nanotubes stabilized with 4-(pyrrole-1-yl) benzoic acid (PyBA) active towards glucose oxidation.

The presence of 4-(pyrrole-1-yl) benzoic acid in such integrated systems improves their stability and introduces new functional (carboxyl) groups which play an important role in the enzyme immobilization on surfaces of such layers. Systems with controlled composition and physicochemical properties act as good carriers and mediators for enzymes and other catalytic redox centres.

As a redox mediator, tetrathiafulvalene (TTF) has been used. The presence of TTF facilitates the effective flow of electrons from redox centres of the enzyme (glucose oxidase) to the glassy carbon electrode. Carbon nanotubes in such systems plays an important role, forming a three-dimensional "nanowire” network around the enzyme molecule, as well as they improve electronic conductivity of the bioelectrocatalytic layer. Combination of glucose oxidase, carbon nanotubes and the appropriate redox mediator has produced a system capable of effective oxidation of glucose in 0.1M phosphate buffer (pH = 7.0).

The problem of hydrogen peroxide (which is a product of glucose oxidation) has also been addressed. The use of horseradish peroxidase (HRP) and catalase (CAT), i.e. enzymes capable of H$_2$O$_2$ decomposition has led to increase of the overall catalytic activity during electrooxidation of glucose and shifted the oxidation potentials towards more negative values.

The proposed integrated electro-active systems towards glucose oxidation in neutral environment seem to be of great importance to the development of biofuel cells.

20:00 Poster 07

Development of electrocatalytic materials based on the mixed addenda Dawson heteropolyanion and conducting polymers

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Over the last several years, there has been a growing interest in heteropolyanions (HPAs), especially in the field of chemically modified electrodes owing to reversible redox activities of HPAs and their excellent electrocatalytic properties towards a range of substrates like nitrite [1]. They also exhibit fast mediating capabilities during electroreductions [2]. An important aspect of an electrochemical based sensor is the successful immobilisation of the electrocatalyst on the electrode surface. Several techniques such as layer-by-layer assemblies [3], incorporation into polymeric films [4] have been employed to attach HPAs to different surfaces. Here we report a comparative study concerning the immobilisation of the Dawson type mixed addenda HPA, $[P_2W_{17}VO_{62}]^{8-}$ in different conducting polymers, such as polypyrrole, PPy, poly(3,4-ethylenedioxythiophene), PEDOT, poly(2, 2'-bithiophene), PBT.

Functionalisation of conducting polymers, CPs by the incorporation of different functional molecules develops their functions. In addition, CPs are considered to be suitable matrices as their conductive properties and compabilities to molecule and ions may be used to convey the electronic structure and properties of the immobilised species. The $[P_2W_{17}VO_{62}]^{8-}$ was chosen in this study because V-substituted Dawson-type HPAs were previously presented as versatile electrocatalysts. Moreover, the presence of V atom(s) within the Dawson type V-substituted HPAs was shown to be beneficial in driving their pH stability domains towards high values [5].

The $[P_2W_{17}VO_{62}]^{8-}$ was successfully immobilised in PPy films. These films were stable at pH 2 and 7 upon continuous potential cycling through $V^{5+/4+}$ redox process. However, in the negative potential region where the polymer backbone was reduced, the HPA leached out of the film. Investigation of the other conducting polymers, i.e. PEDOT and PBT proved valuable. Especially, in the case of the former polymer, the film was stable in the negative potential window as PEDOT remained in conducting state. Consequently it was possible to view the tungsten-oxo redox processes clearly defined. Furthermore, the electrocatalytic properties of the formed films were investigated. For instance the $[P_2W_{17}VO_{62}]^{8-}$ – PPy hybrid films showed electrocatalytic activity towards the oxidation of ascorbic acid. Therefore, applications of the investigated systems in the electrocatalysis and analytical sensing can be predicted.

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20:00 Poster 08

Identification of pure pharmaceutical substance (ibuprofen) and its modification masking substances with the use of electronic tongue

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Electronic tongue is an array of sensors (usually electrochemical sensors), used for analysis of complex liquid simples [1]. The analysis of the signals can be performed by PCA (Principal Components Analysis) and other numerical methods. This kind of device allows to recognize the components and taste additives in pharmaceutical products [2].

Ibuprofen is used in medical syrup for children however, it exhibits bitter taste. In order to mask it Hypromellose and Eudragite can be used to modify its flavour.

In this work we present the preliminary studies on the recognition of ibuprofen and ibuprofen modified with taste masking substances with the use of electronic tongue. Potentiometric ion-selective electrodes with PVC membranes (Na^+-, K^+-, NH_4^+-, Ca^{2+}-, amine ions-, CO_3^{2-}-, cation-, and anion-selective) were applied in stationary measurements of the samples.

The obtained sensor signals were processed by Principal Components Analysis (PCA) and are presented in Figure 1. It was found, that the presented electronic tongue was capable of the discrimination of pure ibuprofen and ibuprofen modified with two taste-masking substances.

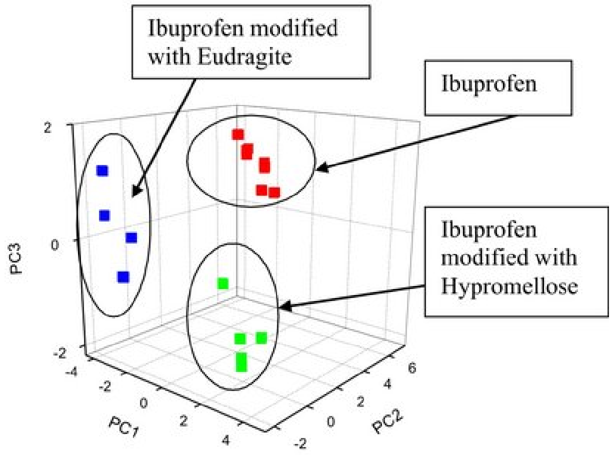

Figure 1. PCA plot of ibuprofen and ibuprofen modified with taste additives (Hypromellose and Eudragite).

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Programme and by Project MNS-DIAG Nr POIG.01.03.01-00-014/08-00

20:00 Poster 09

Distance dependence in peptide-mediated long range electron transfer

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We present the peptide molecules which act as a mediator for long range electron transfer. Understanding the role of peptides in bridge-mediated tunneling of electrons is essential from biological point of view but is also very important for the development of biosensors and nanotechnology. Investigation of electrical properties of single molecules is of special interest because of their potential application in molecular electronics. In some cases we observed the current rectification.

We designed and synthesized 4 thiolated peptide derivatives containing from 1 to 4 proline residues and used them for preparation of self-assembled monolayers (SAMs) on gold electrodes. The quality of the resulting layers and the SAMs coverage were examined using electrochemical impedance spectroscopy and cyclic voltammetry. The electrical behavior of gold-molecule-gold junctions incorporating these peptides was investigated using scanning tunneling spectroscopy (STS). The STS method allows to measure the conductance of a single molecule entrapped in a molecular junction. It also provides the information about the influence of the length and the secondary structure of the molecule on electron transfer efficiency.

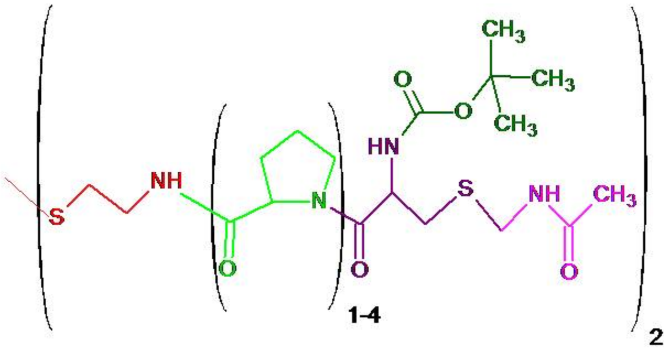

Fig.1 Structure of the synthesized peptide consisting of L-proline and L-cysteine with protected thiol and amine groups and a cystamine linker.

20:00 Poster 10

Influence of three oxicam drugs on the properties and enzymatic lipolysis of model membranes

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Nonsteroidal anti-inflammatory drugs (NSAIDs) are among the most widely used medications in the world because of their high efficiency in reducing pain and inflammation [1]. The basic mode of their action is inhibition of the pro-inflammatory membrane enzyme cyclooxygenase (COX) [2]. Some highly potent of NSAIDs belong to the oxicam group: meloxicam (MEL), piroxicam (PIR), and tenoxicam (TEN); these drugs have different biological effects despite their similar chemical structures. Because the prerequisite for accessing the cyclooxygenase by the drugs is interaction with the membrane, the focus of the current study was a comparison of how MEL, PIR, and TEN interact with model biological membranes.

In this research, model membranes formed with different phosphoglycerides were studied using Langmuir technique upon interaction with TEN, PIR, and MEL. Changes of the phospholipid monolayer properties induced by the oxicam drugs were studied with surface pressure and surface electrical potential, polarization modulation infrared reflection absorption spectra, Brewster angle microscopy and phospholipase A2 (PLA2) activity [3]. The monolayer experiments demonstrated significant differences between the interfacial properties of MEL, PIR and TEN. Indeed, the results obtained show that MEL has the highest ability to modify membrane fluidity and surface potential, followed by PIR and TEN. Additionally, the lipolysis experiments show that PLA2 activity is different upon interaction with the three drugs; it decrease more significantly in the presence of MEL compared to the other two oxicams. We suggest that the least polar MEL penetrates more easily to the film compared to PIR and TEN, and the effects observed are proportional to the amount of the oxicams present in the film. Moreover, the overall results indicate that the oxicams interact both with the apolar methylene and with the polar carbonyl groups; this leads us to think that the oxicams are localized between the lipid hydrocarbon chains and the polar heads in the monolayer. It can be expected that the capacity of the NSAIDs to penetrate into the lipid layer is crucial for accessing and inhibiting COX-2 and, consequently for the therapeutic efficiency of the three oxicams.

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Acknowledgments: This work is supported financially by the Ministry of Science and Higher Education, Grant No N N204 147537.

20:00 Poster 11

Selective complexation of inorganic cations with two amphiphilic calixarene derivatives in Langmuir films

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Two new amphiphilic p-tert-butylcalix[4]arene derivatives were investigated in order to understand two important features of ionophores, namely ion complexation and the possibility of incorporation or translocation across biological membranes [1, 2]. The derivatives used have one or two nalidixic acid moieties grafted at the calixarene lower rim.

In this study Langmuir films of two calixarene derivatives were formed on pure water and on aqueous solutions of mono- and divalent metal chlorides: LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $CuCl_2$, and $ZnCl_2$. The complexation properties were studied using surface pressure and surface potential measurements, as well as Brewster angle microscopy and polarization modulation infrared reflection-absorption spectrometry. The compression isotherms were determined as a function of salt concentration using aqueous solutions in the range $5\cdot10^{-6}$ to $5\cdot10^{-2}$ M. On the other hand, the compression experiments were performed at different temperatures: 20, 25, 30, 37, and 40 °C giving access to a thermodynamic analysis.

The compression isotherms of the monolayers formed on different subphases show differentiation between the monovalent and divalent cations with both calixarene derivatives. This differentiation was interpreted in terms of conformational changes occurring in the ligands upon complexation. The differences of the conformations of the mono- and divalent cation complexes may be important from the point of view of the interactions with lipid membranes and the biological activity of these potential ionophores.

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20:00 Poster 12

Integrated carbon nanotube based mediating systems for bioelectrocatalysis: application to oxygen reduction and glucose oxidation

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In our research we have exploited unique electronic and mechanical characteristics of multi-walled carbon nanotubes (MCNTs) to construct the efficient anodic and cathodic bioelectrocatalytic materials for biofuel cell applications. To stabilize composite films, we utilize MCNTs modified with ultra-thin layers of organic (e.g. 4-(pyrrole-1-yl) benzoic acid [1]. We expect here attractive electrostatic interactions between anionic adsorbates and positively charged domains of the enzymatic sites. Other important issues are stability and mediating capabilities of adsorbates. We have also utilized metalloporphyrin redox centers (at which the reduction of oxygen, mostly to hydrogen peroxide, is initiated) and such an enzyme as horseradish peroxidase (HRP), or cabbage peroxidase (CP), that is capable of catalyzing electroreduction of hydrogen peroxide to water as a final product. Co-existence of the above components leads to synergistic effect that is evident from some positive shift of the oxygen reduction voltammetric potentials (more than 50 mV in citrate buffer) and significant increase of voltammetric currents (relative to those of the enzyme-free system). The film has also exhibited relatively higher activity towards reduction of hydrogen peroxide. It is reasonable to expect that the reduction of oxygen is initiated at cobalt porphyrin redox centers, and the undesirable hydrogen peroxide intermediate is further reduced at the horseradish or cabbage peroxidase enzymatic sites.

The development of bioanode has also been investigated. To facilitate electron transfer between the electrode surface and the redox protein centers, the concept of co-deposition of MCNTs within the bio-electrocatalytic film has also been pursued here. First, MCNTs have been modified with ultra-thin layers of tetrathiafulvalene (TTF) to form stable colloidal suspensions of carbon nanostructures [2]. They have been utilized to produce Nafion-containing inks for sequential deposition of components. The presence of TTF is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode. TTF and its derivatives constitute a group of redox molecules that were successfully used as redox mediators in the enzyme electrochemistry. As before, MCNTs have supported transport of electrons within the bio-electrocatalytic film. Our highly MCNT-based porous films have presumably acted as three-dimensional network of nanowires around the enzyme molecules and have promoted the efficient electron transfers. Thus we have produced a catalytic system capable of effective oxidation of glucose in 0.1 M phosphate buffer (pH = 7).

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20:00 Poster 13

The investigation of masking effect of Eudragite with ISE array

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Most of the medicine substances exhibit strong bitter taste, that can negatively influence patient attitude to realized therapy. A special attention is given to taste of drugs devoted to small children, because it is essential for this group of patients. Pediatric orally taken drugs should be liquid, easily to be measured by volume and without taste that cause vomit reaction. Moreover, they cannot exhibit pleasant flavor, in order to prevent overdosing. One of taste masking methods of medicines, also changing its releasing profile, is the covering particles consisting heal substances.

Electronic tongue can be one of diagnostic technique, that allows for repeatable *in vitro* taste analysis. It's a device simulating human sense of taste, that allows identification and classification of liquid samples. Usually, these systems are not used for selective chemical compound detection, but to the recognition of sample properties. Taste is not linearly dependent from chemical composition, and particular relations between compounds are not obvious although, there are some known relations, however like bitter taste masking effect by some sweet taste substances.

In this paper Ion-Selective Electrode (ISE) array was applied to the analysis of drug substances with and without taste modification. Classic ion-selective electrodes with selectivity towards lipophilic cations and anions, Na^+, K^+, Ca^{2+}, NH_4^+, amines and carbonate ions were used in stationary mode of measurement. Sensors signals created chemical image of pure medicine samples (Roxithromycin and Ibuprofen) and medicines, which taste was masked by Eudragite and Hypromellose. Thanks to Principal Component Analysis (PCA, Figure 1) it was possible to distinguish medicine samples by the presence of changing-taste substance criterion/standard. It was noted that modification by Eudragite caused similar change on Roxithromycin and Ibuprofen. The obtained results showed, that electronic tongue can be used for analysis of masking effects in drugs.

ACKNOWLEDGEMENT

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20:00 Poster 14

Design and synthesis of libraries of artificial enzymes

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Based on the observation that process of binding ligands by artificial receptors formed be self-organisation of *N*-lipidated peptides immobilized on the cellulose is reversible we designed catalytically active structures by incorporation into the peptide fragment amino acids sequences characteristic for enzymatic active sites. Designing the catalytic structure we learned lesson from Nature, expecting several advantages arisen from positioning of the substrate inside of the binding pocked of catalytically active moiety. We expected, that contrary to the most of man-made catalysts designed in accord to the concept of close contact of the substrates located in the outside of catalytically active core structure, catalytic monolayer of *N*-lipidated peptides immobilized on cellulose *via* triazine scaffold would act much more efficiently and selectively, resembling enzymes. In the consequence of this conceptual approach, the catalytic processes may proceeds in the most suitable microenvironment, under milder conditions, much faster and with exceedingly high regio-, chemo-, and stereoselectivity.

Catalyst were prepared [1] by self organization of podands prepared from *N*-lipidated oligopeptides tethered in the regular fashion to the cellulose *via* linker made from fenylenediamine and 2,4-dichloro-6-methoxy-1,3,5-triazine. For assembling of the all elements of the podands, triazine coupling reagents were used [2] in all coupling steps.

The library of highly potent artificial esterases was prepared by incorporation into the peptide fragment residues of catalytic triade His, Ser, Asp (Glu). The activity of catalysts has been confirmed by hydrolysis and alcoholysis of *p*-nitrophenyl esters of *N*-protected di- and tripeptides.

Recently, we found that general approach presented above can be applied also for designing the library of artificial isomerases catalyzing *O→N* (*N→O*) isomerisation of *N*-benzoyl-2-phenylisoserine , side chain of Paclitaxel and carboranes.

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20:00 Poster 15

Nanofiltering membrane sensors for the determination of homologous polyoxyethylated nonylphenols

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Recently nonionic surfactants have found a wide application in various industrial fields, for example in production of synthetic detergents, drugs, foodstuffs et al. Synthetic surfactants is the mixtures of their isomers, homologues and oligomers. Therefore the quantitative identification and separate determination of them in complex liquids is a difficult analytical problem.

The potentiometric solid-state membrane sensors based on tetraphenylborate salt of the barium complex with poly(oxyethylated alkylphenols) were constructed for the detection of nonionic surfactant in various objects. For separation of homologous nonylphenol (NP) polyethoxylates a surface of poly(vinyl chloride) (PVC) plasticized membranes were modified by molecular PVC-sieves (nanofiltering membranes) with a controlled pore sizes. The different membrane compositions and pore generators were studied. They differed in polyethoxylate NPs with 10 or 100 ethylene oxide units (EOU) used in the membrane and sieve preparation. The main electrochemical characteristics of surfactant sensors with different membrane composition and sieve pore generators were determined. The electrode functions for the membranes work well in solutions of NP ($1\times10^{-5} – 1\times10^{-2}$ M), the slopes being close to the theoretical ones for bivalent ions.

The separating power of nanofiltering membranes was examined at study of the transport processes (diffusion mass transfer) in a two-compartment cell (NP solution with a certain concentration against distilled water) with different molecular sieves between. The values of permeability coefficients and ion flows for nanofiltering membranes were calculated at the same time the NP concentrations in source-solution and pore generator sizes were varied. As the number of ethylene oxide units in nonionic surfactant increases, the said characteristics decrease as shown in Fig.1. Nanofiltering membranes let pass those NPs whose molecules are smaller or comparable in size with the pore generator; bigger ions are retained therefore the express step-down motion of permeability coefficients and ion flows are observed.

The application of nanofiltering membranes improves the selectivity of nonionic surfactant sensors and allows the separate determination of homologous nonylphenol polyethoxylates in mixtures.

20:00 Poster 16

Pyrolyzed polypyrrole-metal composites immobilized on glassy carbon for gas sensing and catalytic applications

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The electrocatalytic application of novel electrode surfaces obtained by thermal treatment of polypyrrole-Co/Mn/Fe composites electrochemically synthesised on glassy carbon has been investigated using the oxygen reduction reaction. Carbon nanotubes (CNTs) were synthesized on glassy carbon by iron catalysed chemical deposition of acetylene vapour. The CNTs were then functionalized by treatment with nitric acid vapour. This was followed by sequentially controlled immobilization of polypyrrole, and dosing of metal (Mn, Co, Fe) particles, alter-nately, by electropolymerization and electrochemical reduction respectively. Electrochemical characterization by cyclic voltammetry and hydrodynamic linear sweep voltammetry shows that the immobilized polypyrrole-metal composites inherently catalyse the electroreduction of oxygen under acidic conditions. The activity of the composites is significantly augmented albeit with diminished stability, by pyrolysis at high temperatures (500^{o}C-850^{o}C) in a conti-nuous flow of nitrogen. An insight into the nature of the active sites of both the unpyrolyzed and pyrolyzed composites is suggested based on transmission and scanning electron microscopic imaging (TEM and SEM), energy dispersive X-ray (EDX) and X-ray photo-electron spectroscopy (XPS) studies. This work presents a new approach for the synthesis of electrocatalytic surfaces with potential applications in fuel cells and gas sensors, for example biological and chemical oxygen sensors.

20:00 Poster 17

Surface Immobilization of Dinuclear Ruthenium Complexes Bearing Aqua Ligand on ITO or TiO_2 Electrode: Fabrication and Its Photoelectrochemical Properties

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Mimicking the natural photosynthetic system is one of the most important targets of supramolecular assemblies on surface to convert sunlight into stored chemical energy. With the idea of realizing photoelectrochemical energy conversion systems, the construction of photoelectrochemical oxidation catalytic system on surface has recently attracted significant attention. In this presentation, we present the syntheses and surface immobilization of novel dinuclear Ru complexes which consist of two separated functional moieties; *i.e.*, one is photosensitizer and the other is oxidation catalyst. Ru-aqua complex as a catalytic site (Ru1) and a Ru-polypyridyl unit as a photosensitizer (Ru2) were bridged by bis(terpyridyl)benzene as shown in Fig 1, in which four phosphonate groups act as a anchor for the surface immobilization on ITO or TiO_2 surface. Cyclic voltammogram of 1 on ITO electrode was shown in Fig.2. Two oxidation processes were observed at +0.75 V and +0.96 V *vs* Ag/AgCl. A surface coverage of 1 was 5.1×10^{-11} mol cm^{-2}(=3.3 nm^{2} $molecule^{-1}$), which suggested that the complex was closely packed SAM of 1 on the ITO electrode. Photoelectrochemistry of 2 on ITO and TiO_2 electrodes was measured in 0.1 M $NaClO_4$ aqueous solution. Steady-state photo anodic current was observed for the complex 2 immobilized on TiO_2 electrode. This preliminary result is promising for the development of new photoelectrochemical catalyst.

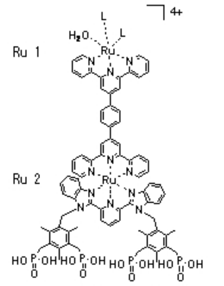

Fig. 1 complex 1 L-L = bpy

2 L,L = H_2O

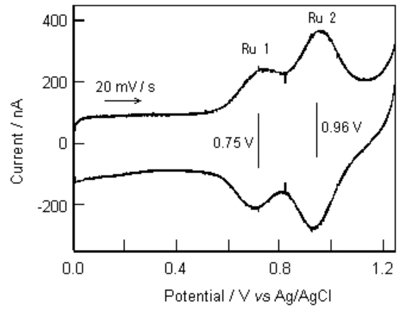

Fig. 2 Cyclic voltammogram of complex 1 on ITO (C.E.: Pt, electrolyte: 0.1M $NaClO_4$ aq.)

20:00 Poster 18

Direct electrochemistry of cellobiose dehydrogenase for applications in the third-generation biosensor and biofuel cell

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Constructing biofuel cells and third-generation biosensors requires direct electron-transfer (DET) reactions, in which the electron transfer occurs directly between enzymes and electrodes. However, DET has been generally proven for a restricted number of redox enzymes which contain a catalytic domain and additionally a redox domain carrying metallocenters such as heme. One of these multidomain enzymes is cellobiose dehydrogenase (CDH). CDH is an extracellular hemoflavoenzyme, which is secreted by various cellulolytic fungi in the course of cellulose degradation. The CDH carries a flavin and a *b*-type heme in two separate domains. The flavin domain of basidiomycete CDH (class I) oxidizes the reducing-end group of cellobiose and higher cellooligosaccharides to their corresponding δ-lactones. The electrons are loaded from the flavin domain to some electrodes via the heme domain. In this study, DET-type bioelectrocatalytic oxidation of CDH from the basidiomycete *Phanerochaete chrysosporium* using carbon nanoparticles is reported. CDH was adsorbed onto carbon electrodes with carbon black (CB) (PRINTEX®30, Degussa). CB powder was mixed with DMF (80 : 20, w/w) to prepare a CB slurry. The slurry was applied to a carbon electrode and dried in a drying oven at 60 °C. A CDH solution was then cast on the CB-modified electrode. We have also investigated the optimal conditions of this CDH electrode. The CDH electrode was employed in the third-generation biosensor based and biofuel cell.

20:00 Poster 19

A biosensor for detection of Mycobacterium tuberculosis siderophores

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One in three people on earth are living with latent *Mycobacterium tuberculosis* (*Mtb*) infection. Every year 8 million more people develop active tuberculosis (TB) and 2 million die from the disease. Iron is an essential nutrient for the growth and pathogenesis of *Mtb* and is required for the function of many important enzymes and metabolic processes. *Mtb* uses iron-chelating molecules called siderophores to remove iron from the host. Although siderophores are required for *Mtb* virulence[1], they have never before been detected in vivo and their precise role and level of expression in TB disease remains elusive. An electrochemical biosensor is proposed for the detection of these siderophores to elucidate their role and quantitatively test for their presence in diseased tissue and clinical samples. This technology could ultimately lead to new diagnostic tools for detection of *Mtb* infection.

Mtb produces two principle types of siderophores: the lipophilic 'cell-associated' mycobactins[2], and the relatively water-soluble carboxymycobactins[3,4]. The variability of the long fatty acid component of their structures makes them a challenging detection target. Lipophilic mycobactins were extracted from Mtb culture supernatants and cell pellets and analyzed by HPLC-MS to identify the primary species of mycobactins produced. Supernatant extracts yielded the greatest quantities of mycobactins. Lipophilic mycobactins have previously been shown to diffuse freely in and around macrophages[5], suggesting that they may be transported out of TB-infected cells and could be detected in tissues of infected individuals.

Lipocalin 2 (Lcn2) is a human neutrophil protein that has been shown to bind the carboxymycobactins of *Mtb*[6] and has been chosen as the receptor for mycobactin capture as part of the biosensor. For this project, Lcn2 was cloned from the human cDNA and expressed in BL-21 cells with a hexahistidine tag on the N-terminus. This tag will be used to anchor Lcn2 to the electrode surface.

Separate experiments indicated that the specific reduction-oxidation activity of ferric iron bound to mycobactin can be successfully interrogated using cyclic voltammetry. This was performed on a glassy carbon electrode in a 1:1 ethanol:PBS solution containing 100 mM potassium chloride and 1 mM ferric mycobactin J (MJ, Allied Monitor).

This evidence supports the feasibility of a biosensor for rapid detection of *Mtb* siderophores. Testing of clinical samples could lead toward applications of this sensor as a low-cost diagnostic tool for TB diagnosis in resource-poor settings.

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20:00 Poster 20

Application of metalloporphyrin-based acetate-selective electrodes in FIA systems

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Metalloporphyrins emerged recently as particularly interesting ionophore species[1]. The selectivity pattern of this group of ionophores is significantly different from the sequence based on ions free energy of hydration (so-called Hofmeister selectivity pattern[2]). It was shown that the unique potentiometric selectivities observed for membranes doped with various metalloporphyrins result from selective interaction of analyte anion with the metal center of the porphyrin structure. Metalloporphyrin – based ISEs could serve as detectors in flow injection analysis (FIA) systems. Example of such system is setup developed for glucose determination with metalloporphyrin-based polymeric-membrane ISE selective to fluoride as a detector[3].

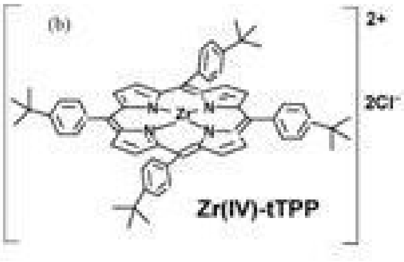

Fig. 1. Structure of dichloro[5,10,15,20-tetra(tertbutylphenyl)porphyrinato]zirconium(IV).

The scope of this work was to study the influence of porphyrin structure and polymer membrane composition on the acetate response of ISEs doped with Zr(IV) – porphyrins. Among few tested ionophores, the best response parameters (selectivity, sensitivity, LDL) towards acetate were obtained for electrodes with membranes containing Zr(IV)-tTPP (see Fig. 1). Electrodes with membranes based on the chosen compound were then used as detectors in FIA systems for acetylcholine determination and acetylcholinesterase inhibition studies.

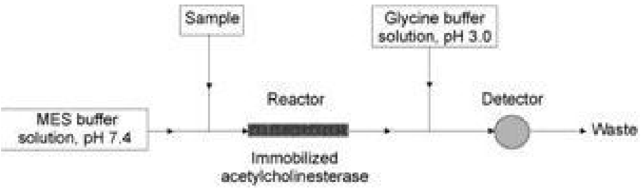

Fig. 2. FIA measurement setup for acetylcholine determination used in this work.

The method based on the enzymatic hydrolysis reaction, where choline and acetate are produced, was applied for acetylcholine determination. Enzyme (acetylcholinesterase) was covalently immobilized on amberlite XAD7 and placed in PVC tubing forming flow-through reactor. Newly designed system (see Fig. 2), is the only one, described in literature to date[4], that uses potentiometric detection of acetate for acetylcholine determination. Proposed FIA system allowed for determination of acetylcholine in the range of 10^{-4} to 10^{-1} M, with the throughput of 60 samples per hour. The lifetime of enzymatic reactor was approximately 9 days. The electrode response parameters stayed unchanged during this period.

The same system was used for determination of chlorpyrifos – the organophosphorus insecticide compound which can function as inhibitor of acetylcholinesterase, resulting in decrease of acetate-dependent signals. The preliminary studies showed that such system allows for determination of inhibitor compound at the level of 10^{-5} M.

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20:00 Poster 21

Structure-reactivity effects in electrocatalytic dioxygen reduction in aqueous solutions at electrodes coated by electrochemically synthesized molecularly imprinted polymers of a cobalt porphyrin diphenylamine derivative

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Three different structural modifications of the *tetrakis*-[4-(N,N-diphenylamino)-phenyl]porphyrinatocobalt(II), (Ph$_2$N)$_4$CoP, polymer were prepared with the aim of developing an efficient electrocatalytic material for dioxygen electroreduction in aqueous solutions. The polymers were deposited on electrodes as thin films under cyclic voltammetry (CV) conditions by electrochemical polymerization of the (Ph$_2$N)$_4$CoP monomer or its complex either with a monodentate or bidentate cyclic amine ligand. A blank polymer film, prepared from genuine (Ph$_2$N)$_4$CoP under anaerobic conditions, served as the control. The bidentate ligand, vis. piperazine, was used as a template to form in solution a sandwich type stacked (Ph$_2$N)$_4$CoP complex while the monodentate ligand, vis. 3-bromopyridine, to form a non-stacked reference complex. Subsequently, the complexes were oxidatively electropolymerized to form a structured and non-structured, respectively, molecularly imprinted polymer (MIP) films. Then, the ligands were extracted from these films with acidic aqueous solutions. The presence of the axially coordinating ligand in the MIP film before and its absence after the extraction was confirmed by measurements of UV-vis absorption spectroscopy and XPS. Next, dioxygen was electrocatalytically reduced at the polymer film-coated electrodes. Integrity of the polymers was examined by SAXS and UV-vis reflection spectroscopy. Differences in the Soret band positions indicated structural differences between the structured and non-structured MIP films. The AFM imaging showed higher relative roughness of the structured than both the non-structured and pristine monomer containing polymer films. The electrocatalysis was examined for different pH aqueous buffer solutions under conditions of both CV at a stationary glassy carbon (GC) disk electrode and voltammetry at a rotating GC disk and a Pt-GC ring-disk, electrode. The structured MIP film appeared to be the most efficient catalyst for dioxygen electroreduction both in acidic and neutral solutions of promising ultimate application as a durable cathode material for fuel cells.

20:00	Poster	22

Restructuring and cleaavage of ferrocene-alkanethiol ester SAMs in lipase-based activity assays.

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Electrochemical activity of ferrocene (Fc)-terminated SAM of alkane ester immobilised on gold electrode is shown to depend on the buffer conditions used. It is demonstrated that upon electrochemical activation in phosphate buffer solutions and further in sulphuric acid solutions the SAMs undergo restructuring, which stabilises the signal from the Fc groups and exposes the internal ester groups to the SAM/solution interface. The restructuring of the SAM enables efficient hydrolysis of the ester bond by lipase enzyme accompanied by the release of the part of the Fc redox active groups from the electrode surface, thus decreasing the electrochemical signal from the surface-confined Fc groups. This reaction was used in electrochemical sandwich DNA hybridisation assay with lipase as a label.

20:00	Poster	23

DNA repair enzymes and bioelectronic devices

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The subgroup of DNA repair enzymes known as DNA photolyases are well known for their light-elicited catalytic activity which repairs ultraviolet radiation-generated cyclobutane pyrimidine dimers (CPD) in DNA. In this mechanism, DNA photolyase absorbs blue light which elicits a hypothesized single electron transfer (SET) event from the flavin adenine dinucleotide (FAD) cofactor in DNA photolyase to the bound CPD- containing DNA. The electron transfer results in the chemical separation of the pyrimidine bases and the electron transfers back to the FAD cofactor. In this communication, preliminary models for the use of DNA photolyase SET in bioelectronic sensing are discussed. Experimental evidence that suggests engineered DNA photolyase has DNA repair activity is reported. Models regarding the binding of DNA photolyase to conducting and semiconducting electrodes are discussed.

20:00	Poster	24

The interactions between methylene blue and various types of DNA at screen-printed electrodes

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Methylene blue (MB), a dye belonging to phenothiazinum family is one of many molecules showing high affinity to nucleic acids as they interact with DNA by several mechanisms [1]. Even though MB is typically used as a photosensitizing agent and a DNA hybridization indicator, its modes of interaction with the DNA molecules are not clearly described. Various experimental studies carried out using spectroscopic and electrochemical techniques [2], and also theoretical calculations [3] have lead to the conclusion that the dye intercalates between the bases, mainly guanine, but other types of interactions such as minor groove binding close to AT sequences and screening of charges of the phosphate groups are also possible.

The interactions between DNA and MB were extensively studied electrochemically using a decreasing reduction peak of MB as useful analytical signal [4, 5]. The goal of our work was to investigate the DNA-MB interactions by monitoring the changes in the MB oxidation signal simultaneously with the MB-DNA complex signal. The home made screen-printed (SP) three electrode system consisting of a graphite working electrode, Ag/AgCl reference electrode and a graphite counter electrode, were used to carry out square wave voltammetric (SWV) experiments. Four types of DNA were used: double stranded salmon testes DNA (dsDNA) as an example of chromosomal DNA, supercoiled plasmid pUC19 (scDNA) as an exemplary circular structure of DNA, and two 8-mer oligonucleotides – 5’GCGCGCGC3’ [d(GC)$_4$] and 5’ATATATAT3’ [d(AT)$_4$] as a short DNA chains containing only one type of nucleic bases (either guanine or adenine) possible to observe by electroanalysis. After thorough cleaning of the SP electrodes in 0.25 M acetate buffer solution containing 10 mM KCl (pH 4.75), MB aliquots were successively added to the solution, and SW voltammograms were recorded after each addition. The MB concentrations have been changed from 2 nM to 10 µM.

The use of such a wide range of MB concentrations, from nano- to micromolar, to probe the interactions with various types of DNA allowed for the detection and comparison of various signals related to DNA-MB interactions. Except for the presence of a well known MB oxidation peak at ca. -0.2 V vs. Ag/AgCl, another MB oxidation peak has been detected at +0.9 V. These signals increased significantly in comparison to signals obtained in the absence of DNA, thus proving the existence of strong interactions between the DNA bases and MB. The MB oxidation peak currents depended on the type of DNA used. The peak at -0.2 V was 1.7, 2.4, 3.5, 4.3 times higher for dsDNA, scDNA, d(AT)4 and (GC)4, respectively, as compared with the MB peak in the absence of DNA. Similarly, the peak at +0.9 V was 2.2, 2.7, 3.9, 4.6 higher for dsDNA, scDNA, d(AT)4 and d(GC)4, respectively, indicating MB interactions not only with guanine, but also with adenine in these nucleic acids. Moreover, in the case of (GC)4 oligonucleotide, a new peak appeared at ca. 0 V, apparently due to the formation of a complex of MB and guanine.

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20:00 Poster 26

HS-undecylcalix[4]arenes as the receptors for detection of dopamine by quartz crystal microbalances

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Dopamin is neurotransmitter, which play significant role in the functioning of central nervous, renal and hormonal systems. Dopamine is also illegally used in the doping. Its concentration varied from 0,163 nM in the blood to 384-2360 nM in urine. The concentration of dopamine in the extracellular fluid of central nervous system is 0,01-1 μM. Development of sensitive method of detection dopamine is urgently needed for diagnosis and also in the purpose of antidoping tests. Currently the detection of dopamine is based on electrochemical methods, HPLC, fluorimetry and capillary electroforesis.

Our approach is based on the detection of the dopamine by the quartz crystal microbalance (QCM) using thickness shear mode method (TSM**)**. As a receptor we used 25.26.27.28-tetrakis(11-sulfanylundecyloxy) calix[4]arene (calix[4]arene) that has been chemisorbed on a gold surface of quartz crystal resonator. We studied the kinetics of the changes of the series resonant frequency, f_s, and the motional resistance, R_m, of the quartz crystal transducer following addition of dopamine. We observed typically the decrease of f_s and increase of R_m, following addition of dopamine. The increase of R_m suggests on increase of surface viscosity. The changes of both parameters started already at 53 pM of dopamine. The topography of the layers was investigated by atomic force microscopy in taping magnetic mode. The images of the calix[4]arene layers in an air environment revealed smooth surface with irregular pinholes.

ACKNOWLEDGMENTS This work was financially supported by Agency for Promotion Research and Development under the contract No. APVV-0362-07 and by Slovak Grant Agency (Projects No.VEGA 2/7134/27, VVCE-0064-07 M. Š. and No. 1/4016/07 to T.H. The Calixarenes was a gift from Prof. P. Lhoták from Institute of Chemical Technology, Department of Organic Chemistry, Prague, Czech Republic).

20:00 Poster 27

Sorption properties of algae Spirogyra sp. and their use for heavy metals determination in surface water

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At present the classical, instrumental methods of the environment quality investigations are very often supplemented or even replaced by much cheaper biomonitoring ones.

The most commonly used biomonitors of atmospheric aerosol pollution are lichens [1, 2] and for assessment of surface waters contamination algae are frequently utilized [3]. Algae are very good sorbents of heavy metals. Utilization of their sorption properties in phytoremediation is investigated [4].

The aim of our investigations is assessment of algae utilization possibility for fast surface water classification as regards concentrations of heavy metals. In this case the classical AAS spectrometry requires solutions preconcentration.

Our investigation results concern mainly sorption kinetics of selected heavy metals (Mn, Cu, Zn, Cd and Pb) from solutions prepared in laboratory. It was found that after about 30 min sorption efficiency is 90-95 %. After 30 min of algae exposition in water polluted with heavy metals, the increase in metals concentrations in algae is proportional to their concentration in the investigated water sample.

For example, concentration of Cd in algae immersed for 30 min in solution with 0.005 $mg \cdot dm^{-3}$ of Cd (this concentration corresponds to the limit for IV class water) increased from 9.5 $mg \cdot g^{-1}$ d.m. to 17.3 $mg \cdot g^{-1}$ d.m. The standard deviation S.D. < ±10%.

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20:00 Poster 30

Development of mass-detection affinity biosensor for determination of prion proteins using dendrimers as a support for immobilisation specific antibodies

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Prion diseases are a group of fatal neurodegenerative disorders that include scrapie in sheep , bovine spongiform encephalopathy, Creutzfeldt-Jakob disease and Gerstmann-Sträussler-Scheineker diseases in humans . It is suggested that the main reason of these diseases is asssociated with the conversion of the cellular prion proteins (PrP^C) into their misfolded pathogenic isoform PrP^{Sc}. The accumulation of PrP^{Sc} in the central nervous system is the common feature of the prion diseases. So far there is no available effective ante mortem test of the presence of PrP^{Sc}. At the same time, possibility of early diagnosis of prion disease could increase effectivity of the therapy. We therefore focused our work on development biosensors for detection prion proteins. For this purpose we used mass-sensitive affinity sensor based on quartz crystal microbalance (QCM).

Because PrP^{Sc} is highly infectious compound, we have focused on PrP^C detection. The methods of detection of PrP^{SC} and PrP^C is, however analogical. The differences consists in using different antibodies. The PrP^C specific antibodies PRI308 that selective bind to 106-126 amino acid residues of recombinat PrP^C (recPrP) have been immobilised on a surface formed by mixture of with covalently attached neutravidin and tightly adsorbed biotinylated protein A. The protein A due to its natural afinity towards the Fc region of antibodies was used for the oriented immobilization of antibodies. We have shown, that QCM biosensor allowing to detect recPrP with detection limit 4.4 nM, which is sufficient for detection PrP^C in blood (physiological concentrations 20 nM). However further effort would be necessary for development more sensitive method that will allow to detect trace concentration of PrP^{Sc}. These experiments are in progress.Time dependent AFM images performed in solution during interaction of recPrP with the PRI308 suggest that the surface roughness changed during the immobilization process. The integrity of the layer was investigated by cyclic voltammetry at the presence of redox couple $Fe(CN)_6^{4-/3-}$. These measurements indicate that the sensitive layer with the PRI 308 is practically impermeable for redox probe species.

Acknowledgements. This work was financially supported by European Commission under 6 FP program NoE NeuroPrion (Contract No. FOOD-CT-2004-506579), by Agency for Promotion Research and Development under the contract No. APVV-0362-07 and by Slovak Grant Agency (Projects No. 2/7134/27, VVCE-0064-07 and 1/4016/07 to T.H).

20:00 Poster 31

Cyclodextrins as molecular recognition elements in monolayers

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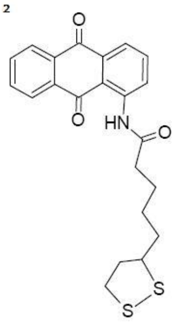
Cyclodextrins are cyclic organic compounds obtained by enzymatic transformation of starch. Among the class of ‘‘host’’ molecules, the β-cyclodextrin is one of the most abundant natural oligomers and corresponds to the association of seven glucose units. The cavity formed has a hydrophobic character, whereas the exterior is strongly hydrophilic. This unusual structure allows various guest molecules to be included in the cavity via non covalent bonds to form inclusion complexes [1, 2]. In the field of environmental research, the inclusion ability of cyclodextrins has attracted considerable attention due applications in sensing devices and the construction of molecular machines, which are able to perform tailored mechanical tasks [3, 4, 5].

In our project we complexation of β-cyclodextrin with 1-aminoanthraquinone in solution and with self-assembled monolayers of lipoic 1-anthraqunoneamide **(2)** is studied using cyclic votlammetry. We confirmed the complexation of 1-aminoanthraquinone by β-cyclodextrin using spectrometric and spectrofluorimetric methods. We also investigated the electrochemical behavior of self-assembled monolayer of non-electroactive lipoic 1-adamantaneamide **(1)** in the presence and absence of electroactive mono-6-thioureido-(1-antraquinone)-per-O-methyl-β-cyclodextrin. For comparison we also studied electrochemical properties of this β-cyclodextrin derivative in solution.

1

2



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20:00 Poster 32

Biosensing Applications Of Engineered Pyranose 2-oxidases Wired With Osmium Polymers

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Pyranose 2-oxidase (PyOx) from Trametes multicolor, a homotetrameric flavoprotein, catalyzes the oxidation of different aldopyranoses at the C_2 to their corresponding 2-ketoaldoses, producing H_2O_2 as a by-product. To make the enzyme communicate with electrodes for applications in enzymatic biofuel cells and biosensors, redox-active polymeric compounds, called mediators, can be used to accomplish mediated electron transfer (MET). Applications of flexible osmium redox polymers have always been promising for such use in enzymatic biofuel cells and biosensors because they allow the formation of a hydrogel and the formal potential can be varied to suit the application and work as an efficient mediator. In this work, rational and semi-rational protein design, based on the crystal structure and on former studies, was used to improve the enzyme's characteristics for use in biofuel cells. In homogeneous steady-state characterization, the resulting mutants (T169G/H450G/E542K/V546C, S113E/T169G/H450G/Q461R/V546C and S113E/T169G/H450G/Q461R/E542K/V546C) showed a significant increase in activity when D-galactose was used as electron donor and either 1,4-benzoquinone or ferricenium ion was used as electron acceptor. The catalytic efficiency increased up to 30-fold. For biosensing applications, these PyOx variants, which showed improved properties for D-galactose as a substrate, were wired with different osmium polymers with formal potentials ranging between -0.140 to 0.270 V. The wild type and the three PyOx mutants and the PyOx were characterized by their pH profile, substrate specificity, and enzyme loading experiments. The kinetic parameters of the biosensing system, maximum reaction rate of the enzyme (V_{max}) and Michaelis Menten constant (K_m), analytical characterizations for different sugars were also determined.

20:00 Poster 33

Local Control of Cell Adhesion by Electrochemically Patterned Oligoethyleneglycol-Terminated Self-Assembled Monolayers

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Site directed adhesion of cells can be obtained by cultivation of adherent cells on patterned substrates containing cell-repellent regions and regions where cells adhere well. Of particular interest are substrates that can be dynamically altered as a cell cultivation experiment proceeds [1-3], for instance in order to introduce new cell types into previously cultured cells.

Patterned oligoethyleneglycol-terminated self-assembled monolayers (OEG SAMs) were created by microelectrochemically formation of Br_2 [4-6]. These substrates were used to monitor local adherence of astrocyts derived from the brains of newborn rats [7] and oligodendroglia OLN-93 cells [8]. These cells adhere without other specific substrate proteins and occupy selectively the manipulated OEG SAM surface.

Bromide is necessary as precursor for the microelectrochemical Br_2 formation used for the modification of the OEG SAM. For the sequential introduction of cells into pre-existing patterns, it is important that adherent cells can withstand bromide concentrations in the culture medium. For that reason, the cytotoxicity of KBr addition to the culture medium (Dulbecco's Modified Eagle's Medium with 10 % fetal calf serum) was tested for OLN-93 cells between 25-100 mM KBr. The results show that these cells can tolerate 50 mM KBr concentration for the duration of 2 hours.

For sequential co-culture experiments on patterned substrates, two clonal cell lines OLN-93 are used: OLN-93 cells transfected with GFP protein and OLN-93 cells transfected with DsRed protein. The local attachment of the different cell populations could be detected by fluorescence microscopy like confocal laser scanning microscopy (CLSM).

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20:00 Poster 34

(Bio)Functionalisation of gold surfaces based on CS_2 – amine reaction

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Several strategies have been employed to immobilise biological compounds onto surfaces for the development of biosensing interfaces. The Self-Assembly method for the anchoring of enzymes or other bio-compounds displays several advantages relative to other approaches, namely, high reproducibility, molecular level control, vicinity from the surface allowing direct electron transfer [1]. In more recent studies [2,3], it has been shown that a variety of secondary amines condense with carbon disulfide (CS_2) onto gold surfaces at room temperature, forming dithiocarbamate monolayers that have been regarded as a versatile chemical alternative for thiols in self-assembled systems [4]. The major structural aspect distinguishing dithiocarbamates from thiolates is the resonance structure among the sulphur atoms, carbon and nitrogen, providing distinct binding properties, namely higher sulphur densities with possible overlapping of molecular and metal states.

The purpose of this work is to use the reaction between CS_2 and amines for direct biomolecule immobilisation onto gold surfaces. To achieve this goal the chemical coupling between carbon disulphide and distinct compounds containing primary (e.g. dopamine) or secondary amines (e.g. tryptophan, hexylmethylamine, epinephrine) have been primarily investigated. Three different approaches were used for the formation of dithiocarbamates on gold (111) electrodes: (i) one pot chemical reaction: gold in contact with a mixture of CS_2 and amines; (ii) self-assembling of a CS_2 monolayer and post-reaction with the amines, and (iii) dithiocarbamate formation through reaction of CS_2 with amines following exposure to the gold surface. The amount of sulphur attached to gold as well as the stability and packing of the monolayers were evaluated by electrochemical reductive desorption studies. In addition, the use of electrochemically active amine compounds (dopamine and epinephrine) enabled to infer on the amount of amines present on the electrode surface, as a result of the successful reaction. Evidence for dithiocarbamate formation has been obtained using the three methodologies, and the modified electrodes were characterised by scanning tunnelling microscopy. Biofunctionalisation of gold surfaces has been also attempted through the reaction of CS_2 with amines present in Glucose Oxidase. Enzyme immobilisation was confirmed through its electrocatlytic response towards glucose.

Acknowledgements

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20:00 Poster 35

Structure of triazole compounds on Ag surface - Raman, SERS, XPS spectroscopy and DFT calculations.

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Molecular structure of 1,2,4-triazole (T), 3-amino-1,2,4-triazole (AT), 3-merkapto-1,2,4-triazole (MT) and 3-amino-5-merkapto-1,2,4-triazole (AMT) adlayers on silver surface was investigated with surface-enhanced Raman (SERS), Raman Scattering and X-ray photoelectron (XPS) spectroscopy and DFT calculations.

To analyze the results, a comparison between the Raman spectra of concentrated, alkalized and natural triazole solutions in H_2O and D_2O and the SERS spectra of adlayers formed in these solutions, measured in situ and in pure NaOH solutions and Raman spectra of sediment precipitated from natural, concentrated triazole solutions after adding $AgNO_3$ have been recorded. These experiments revealed that in adlayers of T the molecules exist as a triazole anions, while AT adlayers contain imino form of molecules deprotonated in the ring . In both monolayers orientation of the ring is more or less parallel to the metal surface. Chemical state of MT and AMT molecules and the monolayer structure depend on monolayer environment. In the sufficiently high concentration and/or low enough pH value of solutions hydrogen atom attached to the pyrrole nitrogen atom is retained and the ring orientation is more or less perpendicular to the metal surface. A decreased concentration and/or an increased pH value of the solution are favourable to the ring deprotonation and in case of AMT also the transformation into the imino form. The change of the ring orientation into more parallel with respect of the metal surface is accompanied by these transformations of the chemical state. XPS spectra proved the existence of an Ag-S bond in all conditions in monolayers of both compounds.

The spectroelectrochemical experiments have also revealed the potential dependence of the structure of triazole monolayers on the electrode. As the changes of chemical state and structure are reversible, the MT and AMT monolayers can be used as a molecular switch.

Quantum mechanical calculation of the vibration energy of triazole-

Ag complexes has allowed assigning their SERS spectra.

20:00 Poster 37

Application of mass fabricated silicon-based gold transducers for amperometric (bio)sensors

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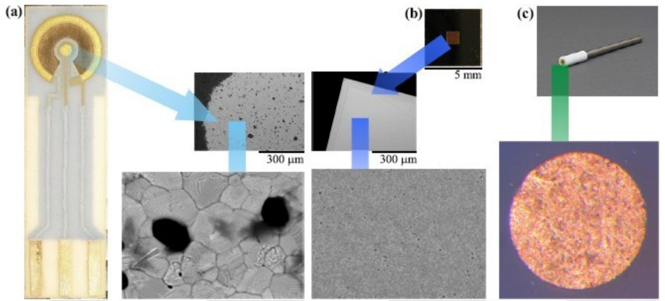
Development of biosensors has increased tremendously over the past few years. The large area of possible applications powers the ongoing research over the immobilization methods of recognition elements, the signal transduction and detection or simply the stability of biosensors in specific environmental conditions.

Thanks to composition of biosensor recognition layer, there is a possibility to investigate various biologically important analytes for example glucose, antigens or DNA. As the nucleotides sequence of the DNA strand may be the indicator of blood contamination with pathogenic bacteria, genetically modified food or mutations being the cause of different genetic disorders, it is one of the most interesting target for biosensors. Since the early stage of any DNA examination techniques, there always was need for good and reliable signal detection methods. These promote the implementation of electrochemical methods in protocols dealing with nucleic acids. The most important advantages of such a methods over the traditional ones are their insensitivity to sample cloudiness, cost effectiveness, operating comfort and most of all the extremely low detection limit.

The surface quality is an important factor affecting results obtained with electrochemical methods especially when self assembled monolayers (SAM) are applied to build recognition layer of a biosensor. In the presented study three types of gold electrode surfaces have been compared, presented in Figure (a-c): commercially available chips with screen printed gold layer (a), silicon chips with vacuum evaporated gold layer and backside contact (b) and typical gold disc electrode (c). For the preliminary examination of the surface roughness the 6-(ferrocenyl)-hexanethiol was chosen as the indicator.



The gold surfaces ware exposed to the 10-3 M 6-(ferrocenyl)-hexanethiol solution. The electrochemical examination was carried out in 50 mM phosphate buffer with 0.3 M NaCl (pH 7.0) as electrolyte. As expected, the best stability and response were obtained on the silicon chips with the evaporated gold layer - probably due to their perfect smoothness compared to screen printed and polycrystalline gold disc electrode. These encouraged us to creation of DNA biosensor based on the silicon chip with vacuum evaporated gold layer. The electrochemical analysis in methylene blue solution of bare gold electrode, with ssDNA and after hybridization ware conducted. The change in height and the potential shifts of reduction peaks of methylene blue due to immobilization and hybridization process corresponds to these well described in literature. Moreover the compact size of our chips allows to significantly reduce the required volume of solutions to be tested.

Acknowledgement: This work was co-financed by the Polish Ministry of Science and Higher Education within a framework of the Operational Programme – Innovative Economy, Priority I, Action 1.3, Sub-Action 1.3.1, Project No. PO1G.01.03.01-00-014/08-00.

20:00 Poster 38

Metallacarboranes as redox labels in voltammetric methods of DNA determination

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There are a lot of different DNA labels [1]. Over last years also boron clusters and metallacarboranes were proposed for the labelling of DNA [2]. Metallabarboranes are vast family of metalocene-type complexes consisting of at least one carborane cage ligand and one or more metal atoms. Many of them undergo reversible chemical or electrochemical oxidation and reduction [3]. This work is a part of the project which aims at the construction of DNA biosensor with voltammetric detection. Electrochemical detection is possible due to metallacarboranes application as a redox labels of DNA.

The goal of this work was:

· Synthesis of 2'-deoxyadenosine – metallacarborane conjugates containing iron or chromium (6-N-{5-[(3,3'-iron-1,2,1',2'-dicarbollide)8-yl]-3-oxapentoxy}-2'-deoxyadenosine **(4)** and -N-{5-[(3,3'-chrom-1,2,1',2'-dicarbollide)8-yl]-3-oxapentoxy}-2'-deoxyadenosine **(5)**) [4, 5].

· Redox activity investigations of compound **4** and **5** using voltammetric methods. Selection of compound with better electrochemical properties to the oligonucleotide – metallacarborane conjugate synthesis.

In the first steps of synthesis, compounds **4** and **5** were obtained. Next, electrochemical investigations were performed. Results allowed to choose compound bearing iron ion (**4**) as a potential nucleic acid redox label. Compund **4** was used in the next steps of synthesis in which H-phosphonate derivative was obtained (5'-*O*-dimethoxytrityl 6-*N*-{5-[(3,3'-iron-1,2,1',2'-dicarbollide)8-yl]-3-oxapentoxy}-2'-deoxyadenosine 3'-*O*-(H-phosphonate)) (**7**). H-phosphonate derivative was used in an trial of oligonucleotide – metallacarborane conjugate synthesis.

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Saturday, 7 November

Morning Session 1

Saturday morning, 7 November, 9:00
Chair: Szunerits, S. Schuhmann, W.

9:00 Tutorial lecture

Moving Scanning Electrochemical Microscopy to Real World Problems

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Scanning electrochemical microscopy has open up new direction for functional characterization of materials for the exploration of new concepts in electrochemistry and for the optimization of sensors and sensor components and biomimetic surfaces.[1] While the initial phase of SECM has seen progress mainly in the establishment of new imaging modes and demonstration of their applicability to classes of problems using well-defined model samples and connection to numerical simulation of idealized experiments, the focus is currently shifting considerably towards more complex samples and less ideal reactions (irreversible reactions in fuel cells and in corrosion). Almost all imaging principles have found application in biochemical or biological context.[2-6] This opens up more direct relation to application but also poses new difficulties for the quantitative understanding of the experiments.[7] New instrumental developments aim for providing complementary information that allows a meaningful investigation of such samples. Critical to the success is the proper choice of control experiments.

This trend will be illustrated by examples for increasing the lateral resolution and the associated differences in maintaining the quantitative rigor of SECM that has been considered as one of its main advantages. A vivid development takes place in the field of new imaging modes that are able to follow irreversible reaction at the sample surface. This is driven by the need of the fuel cell development but also by other application requiring (bio)electrocatalytic reactions of small molecules (O_2, H_2O_2, H_2). In this context pulsed generation-collection experiments[8,9] and local reagent delivery see a revival and expansion[10] and the redox competition is applied in different variations for local analysis.[4, 11] In order to carry out these experiments in a sensible way, patterning of samples with material libraries, e.g. electrocatalysts becomes increasingly important. Many complex materials can only be analysed by using complementing microscopic techniques that provide spatially correlated topographic, optical and reactivity information from exactly the same sample region. In many cases confocal laser scanning microscopy is an interesting complementing technique because of the similar resolution and scanning ranges and because of its ability for mapping three-dimensional concentration distributions.

Finally, analysing samples under conditions that are close to practically relevant conditions but far from ideal SECM imaging conditions is an area where careful judgement between the possibilities and requirements of SECM as a method and the relevance for the application in question must be made.

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9:40 Keynote lecture

Numerical simulation of probing the electric double layer by scanning electrochemical potential microscopy

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Scanning electrochemical potential microscopy (SECPM) has been introduced by C. Li *et al*. (Veeco Inst. Inc.). It was designed mainly to probe the potential profile across the electric double layer by approaching a probe towards charged surface immersed in electrolyte solution. In addition, SECPM offers the possibility to map surface potential of an electrode/electrolyte interface.

Hurth *et al.* reported their EDL potential profile measurements with the SECPM, and concluded that the data did not fit the classical Gouy-Chapmann-Stern (GCS) model. They suggested the need for a theoretical model to explain the measurement process and the effect of the EDL’s overlap on the probed potential. Recently, Baier *et al.* published their results, which concern the surface potential mapping for a single enzyme adsorbed on an electrode. They showed the high spatial resolution which can be reached with SECPM. This can have an interesting advantage comparing to the electrochemical scanning tunneling microscopy (EC-STM) in imaging non-conductive samples.

To our knowledge, a comprehensive theory of SECPM has not been developed, and experimentally this technique to probe the electric double layer is hardly applied yet. We believe that a computational method will help addressing this need for thorough theoretical model. Our motivation is to gain a deeper understanding of the measurement mechanism. The effects of the metallic protrusion of the probe, its open circuit potential (OCP), and the EDLs overlap on the probed potential are studied. A clear Debye screening effect was observed when varying the OCP of the probe. We observed steeper potential profiles for high OCPs due essentially to the electrostatic screening. The dependence on the metallic apex shape was also noticed.

10:00 Short communication

Reactive micropatterned surfaces. In situ substrate modification for biological post-functionalitation by scanning electrochemical microscopy.

Stefania Rapino[1], Giovanni Valenti[1], Massimo Marcaccio[1], Francesco Paolucci[1], Raluca Marcu[2], Marco Giorgio[2]

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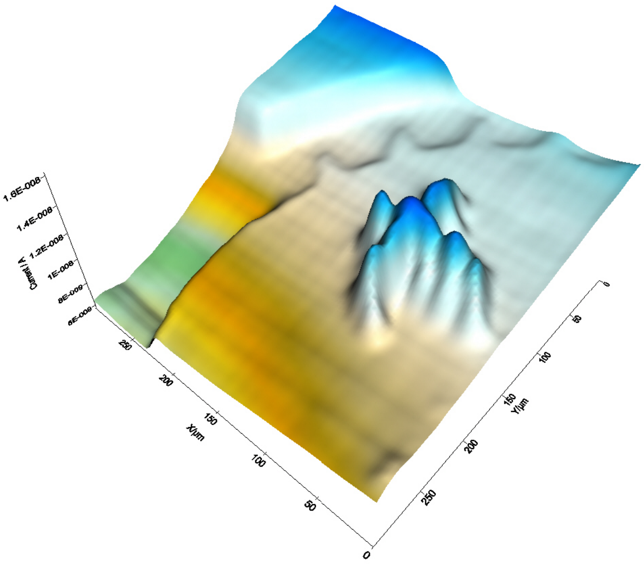
The formation of defined structures on opportune substrates in the micro- and nano-metric scale is one of the major goal of modern science. Moreover, with the aim of miniaturized and integrated device fabrication, it is attractive to realize biological micropatterned surfaces.

Scanning probe microscopy (SPM) has also been considered as a novel instrument for engineering of sophisticated nano and micrometer-scale material and devices. [1] Among various SPMs techniques, Scanning Electrochemical Microscopy (SECM) is a very flexible tool, which can be used for a wide variety of surface analyses; this technique is based on a ultramicroelectrode in close proximity to a substrate, this feature was proven to be a powerful means to obtain surface chemical information of conducting and not conducting surfaces with high spatial resolution. During the past decade SECM has widely used, not only for imaging surfaces, but also for local surface modifications. [2] In the present work we use SECM for in situ surface modification and patterning. Two different methods inducing reactivity in a substrate according to a specific pattern are reported.



The first method is based on local modification of self assembled monolayer (SAM) of thiols on gold. The SECM microelectrode is used for local and defined desorption of thiols. [3] The realized pattern of discovered gold can be then filled with a thiol different from the initial one and holding moieties suitable to fix biological molecules, such as proteins.

The second investigated method is based on direct chemisorption of a synthetic polymer on a conducting surface by *in situ* electrografting. As when the electrode is brought near a conducting surface the electron transfer is confined to a small area on the surface, the SECM microelectrode is used for a local grafting. The electrografted polymer can then be easily post functionalized thanks to a good leaving group on its lateral chains. The substrates can be hence easily used for micropatterning a large variety of molecules. In particular the good capacity of this polymer in anchoring proteins has already been shown. [4]

Using the aforesaid methods we obtained post-functionalizable microstructured substrates, this feature allows to adsorb biomolecule with high control of dimension and geometry of the final pattern.

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10:15 Short communication

Deployment of redox competition scanning electrochemical microscopy (RC-SECM) and an electrochemical robotic system to investigate biofuel cell cathode libraries

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The interest in energy producing devices based on biocatalysts increased notably in the last few years. Either enzymes or microorganisms can be used to catalyse the reactions in the anode or/and cathode compartment of a biofuel cell. Multicopper oxidases like laccases or bilirubin oxidase can catalyse the 4 e^- reduction of oxygen to water at the cathode side. Their efficient and stable immobilisation on the electrode surface conco-mitantly designing optimized electron-transfer pathways between enzyme and electrode is crucial for long-term stability and maximum power output of the envisaged biofuel cell.

One possible approach is the integration of laccases or bilirubin oxidase into an Os-complex modified polymer matrix on top of an appropriate electrode surface. The re-dox potential and the electron transfer characteristics of the Os-complex modified polymer need to be adapted to the chosen enzyme for providing an optimized operation of the biofuel cell. Thus, a specific design of the polymer-linked Os-complexes with respect to their redox potential as well as the properties of the polymer itself is of crucial importance. The redox potential of the polymer-bound Os-complexes can be tailored by variations in their ligand sphere while the properties of the polymer back-bone can be modulated by choosing different types of the polymer-forming monomers. As a matter of fact, by variation of all these parameters libraries of redox polymers are obtained which have to be investigated together with the different enzymes. Thus, fast screening of these multi-parameter systems is essential. In this communication, we will describe the application of redox competition mode SECM (RC-SECM) for monitoring local biocatalytic O_2 reduction activity of enzyme/redox polymer spotsin dependence of enzyme-to-polymer ratio and nature of the used enzyme and/or Os-complex modi-fied polymer. A piezo-microdispenser in combination with a high-accuracy positioning unit was used for automated and reproducible formation of enzyme/redox polymer spot arrays, which were then further investigated using RC-SECM. For a more in depth evaluation of the obtained biofuel cell cathodes, pH and longterm stability was automatically evaluated using an electrochemical robotic system. The enzyme/redox polymer films are automatically formed and fuel cell power and potential curves are automatically obtained using slow-scan linear sweep voltammetry. Results concerning the straight forward and automatic optimization of biofuel cell cathodes by combining RC-SECM and electrochemical robotics will be presented.

COFFEE

Saturday morning, 7 November, 10:30

Morning Session 2

Saturday morning, 7 November, 10:55

Chair: Blanchard, G.J. Oyama, M.

10:55 Keynote lecture

Diamond nanowires: preparation, functionalization and applications

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Boron-doped diamond (BDD) electrodes have received increasing attention because of their excellent electrochemical properties, such as low and stable background current, wide working potential window, high chemical stability, and good biocompatibility. These versatile properties make BDD an excellent candidate for different electroanalytical applications.

Up to now, planar (microcrystalline and nanocrystalline) film electrodes have been the most studied form of diamond electrodes. Even though the electrodes are suitable for many electroanalytical and electrochemical applications, the use of electrode materials with high surface area is very promising for achieving high sensitivity and selectivity. This is can be realized by creating nanostructured diamond electrodes.

Diamond nanostructured substrates are generally obtained by etching BDD electrodes through various masks such as anodic alumina, SiO_2 ordered arrays, Au nanodots, molybdenum, nanodiamond particles, and other materials.

Here, we demonstrate that direct reactive ion etching (RIE) using oxygen of BDD and undoped diamond leads to the formation of diamond nanowires (DNWs). By varying the etching parameters, diamond nanowires of different diameters and lengths are obtained. The resulting surfaces are characterized by scanning electron microscopy (SEM), water contact angle measurements and electrochemical means. The potential of these nanostructured electrode materials for sensing with a high sensitivity is demonstrated in several examples.

11:15 Keynote lecture

End termination of commercial BDD electrodes with Sulphur and Nitrogen functionality for improved immobilisation of biomolecules.

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Commercial boron doped diamond (BDD) electrodes are terminated by hydrogen due to the chemical vapour deposition (CVD) process of and subsequent annealing in hydrogen atmosphere. For most applications in electrochemistry a surface activation procedure is required, which consists of anodic polarization in string acid solution, which reduces the hydrophobic character of the electrode surface. This is followed by cathodic pretreatment under the same experimental conditions but suitably negative voltage in order to enhance the electrochemical response and ensure reproducibility of voltammetric results (1, 2, 3). However, many other kinds of surface modification of BDD electrodes have been attempted, including dry and wet processes, such as thermal, chemical, photochemical plasma etching and electrochemical treatments (4, 5). We have already developed a number of novel conductive polymer platforms for the immobilisation of biomolecules and have demonstrated their electrochemistry and associated applications (6,7,8). In this paper we have concentrated our efforts specifically on the modification of commercial BDD electrodes to enhance its suitability for the immobilization of the integral membrane protein, cytochrome c oxidase, which is composed of several metal prosthetic sites. Immobilisation is proposed to occur through co-ordinate covalent bond formation between BDD electrodes that are S-terminated (or N-terminated) with the metal center of these molecules. In this way the protein is directly attached to the electrode surface and extensive wiring between the active metal centre of the protein and the electrode surface is circumvented. The efficiency of S- and N-termination of BDD electrodes by (i) electrochemical methods and (ii) UV activation was characterised by X-ray proton emission spectroscopy (XPS) and surface morphology was studied using scanning electron microscopy (SEM). The interfacial kinetics of the modified commercial BDD electrodes was studied by various electrochemical methods and will be highlighted in this paper. References: (1) Direct cytochrome c electrochemistry at boron-doped diamond electrodes, F. Marken, C.A. Paddon, D. Asogan, Electrochem. Commun., 4 (2002) 62. (2) V.A. Pedrosa, L. Codognoto, S.A.S. Machado, L.A. Avaca, J. Electroanal. Chem. 573 (2004) 11–18. (3) G.R. Salazar-Banda, L.S. Andrade, P.A.P. Nascente, P.S. Pizani, R.C. Rocha-Filho, L.A. Avaca, Electrochim. Acta 51(2006) 4612–4619. (4) D.A. Tryk, T. Kondo, A. Fujishima, in: A. Fujishima, Y. Einaga, T.N. Rao, D.A. Tryk (Eds.), Diamond Electrochemistry, Elsevier/BKC, Amsterdam/ Tokyo, 2005, Chapter 9. (5) T. Kondo, H. Ito, K. Kusakabe, K. Ohkawa, Y. Einaga, A. Fujishima, T. Kawai. Electrochimica Acta 52 (2007) 3841–3848. (6) J.H.O. Owino, O.A. Arotiba, N. Hendricks, E.A. Songa, N. Jahed, T.T. Waryo, R.F. Ngece, P.G.L. Baker , E.I. Iwuoha. Sensors 2008, 8, 8262-8274. (7) E.A. Songa, V.S. Somerset, T.T. Waryo, P.G.L. Baker, E.I. Iwuoha. Pure Appl. Chem., Vol. 81, No. 1, pp. 123–139, 2009. (8) P.M. Ndangili, T.T. Waryo, M. Muchindu, P.G.L. Baker, C. J. Ngila, E.I. Iwuoha. Electrochimica Acta (2009), doi.org/10.1016/j.electacta.2009.04.058

11:35 Short communication

Electrochemical behaviour of carbonised cellulose nanofibril films on the ITO electrode surface

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Carbon is considered as an excellent electrode material due to its high electrical conductivity and mechanical strength [1]. Pyrolytic carbon films are of interest for use in electroanalysis as they are often cheaper and more versatile as compared to glassy carbon or diamond-like carbon films [2]. The molecular organisation of the precursors is known to affect the structure of the pyrolytic carbon and, therefore, highly organised cellulose is an attractive starting material as a possible source for pyrolytic carbon films on electrode substrates [3]. Cellulose can be degraded to nanocrystalline cellulosic materials [4]. Nanofibrils of cellulose or “whiskers” have been produced previously and they have been deposited on electrode materials using a layer-by-layer film deposition technique [5]. These nanowhiskers are usually obtained by acid hydrolysis of native cellulose of cross-sectional dimensions are typically 4-20 nm and several hundred nanometers long, depending on the source of cellulose [6].

In this study, a novel method was introduced to produce ultrathin carbon layers of cellulose nanofibrils on an ITO substrate. A layer-by-layer deposition technique based on electrostatically driven layering of the cellulose nanofibrils and PDDAC, poly-(diallyldimethylammonium chloride), was employed to build up multilayer films on ITO substrates. Then, the cellulose layers were carbonised by vacuum pyrolysis at 500°C. The film morphology was characterized by AFM studies and the hydroquinone/benzoquinone redox system was employed as a model to investigate the electrochemical properties of these films. The results show that the carbonisation of cellulose nanofibrils changes dramatically the morphology as well as the electrochemical properties of the cellulose films. The number of layers and composition of the film also affect the electrochemical behaviour of the films.

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11:50 Short communication

Hydrogen peroxide sensor based on Ag nanoparticles/ zinc oxide modified electrode

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Due to its wide applications, the determination of H_2O_2 concentration became an important research topic in recent years. Electrochemical sensors based on nanomaterials have been applied to the detection of H_2O_2 [1]. Among various nanomaterials, silver nanoparticles (Ag_{NPs}) with controllable dimension and size distribution attracted much attention because of their excellent catalytic [2] and electric properties [3]. Recently, photochemical reduction of Ag ions, induced by semiconductor materials, is of great interest since the silver loading and overall surface area can be easily controlled by tuning the conditions of the photochemical reaction and the surface morphology of semiconductor template, respectively.

In this study, a Ag_{NPs}/zinc oxide modified electrode was fabricated and its electrocatalytic properties towards H_2O_2 were investigated. The zinc oxide nanorods (ZnO_{NRs}) were first grown onto the FTO glass, which is denoted as ZnO_{NRs}/FTO electrode, covered by a ZnO seed layer by using chemical bath method. Thereafter, the Ag_{NPs} were deposited onto the ZnO_{NRs}/FTO electrode by photo-reducing Ag^+ ions with the aid of UV irradiation (λ=365 nm) for 5 min, donated as Ag_{NPs}/ZnO_{NRs}/FTO. Compared to the ZnO_{NRs}/FTO electrode, a well pronounced peak at -0.62 V (vs. Ag/AgCl/KCl sat'd.) resulting from the reduction of H_2O_2 was observed on the Ag_{NPs}/ ZnO_{NRs}/FTO electrode. Besides, when Ag_{NPs} was deposited onto the mesoporous ZnO film (ZnO_{meso}) in the presence of eosin Y, the resulting Ag_{NPs}/ZnO_{meso}/FTO electrode showed higher catalytic current to H_2O_2 than that in the absence of eosin Y. This behavior can be attributed to the higher loading of Ag_{NPs} on the ZnO_{meso} film. In order to increase the loading of Ag_{NPs}, thus enhancing the sensor sensitivity, the effect of the eosin Y concentration and the conditions of the photochemical reaction were under investigation.

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12:05 Short communication

Positively Charged Surface Functionalised Carbon Nanoparticles as Binding Sites for Redox Active Species

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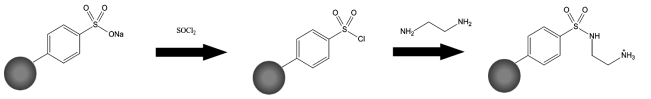
Emperor 2000 carbon nanoparticles are functionalised by a terminating sulfonate group which bares a negative charge. Work has previously been done using a binder mixture of chitosan with these carbon nanoparticles to create a stable film with good conductivity and more useful terminating amine groups.[1,2]



Scheme 1. Functionalisation of the positively charged carbon nanoparticles by a two step synthesis.

This work presents an alternative to the use of binders in which the carbon nanoparticles were directly re-functionalised by a two step synthesis shown in Scheme 1. This has lead to the creation of stable films showing a terminating amine group which can be evaporated onto electrodes and used to strongly bind negatively charged species such as indigo carmine without the need for binding agents.

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12:20 Short communication

Electrochemical growth of alternating Metal/Polymer layers into a colloidal crystal template

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There is a great interest in creating porous materials with 3-dim periodicity as they can be used in very different areas. First of all the increase in active surface area of a porous compared to a flat electrode is desirable for analytical measurements [1,2] as well as for the integration of different materials that can exhibit beneficial catalytic effects [3]. Secondly multiple scattering of light in periodic porous structures can, if certain conditions are met, lead to a photonic band gap in the material, so that the light similar to electrons in a semiconductor cannot propagate anymore in the medium [4,5].

The fabrication of a colloidal crystal template is obtained by the transfer of a Langmuir film consisting of sub-μm Silica particles to a flat Gold electrode [6]. The latter has been hydrophilised by a SAM of an Aminothiol allowing the colloids to be transferred onto the electrode`s surface. By repeating the transfer it is possible to produce a template with a desired number of layers. The bottom up growth into the template is achieved electrochemically either by oxidation of Pyrrole or by reduction of gold ions. Dissolution of the Silica template with hydrofluoric acid generates the inverse structure.

Our goal is to control the electrochemical deposition of PPy and Gold into the template structure, so that a sandwich structure of alternating porous Gold/PPy can be produced that should exhibit special optical properties, as shown in [7].

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12:35 Short communication

FIA detection of nicotine and cotinine using piezomicrogravimetric sensors with zinc porphyrin polymer films as their recognition elements

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Thin films of zinc porphyrin polymers with one or two acetamide “arms” deposited on electrodes by electrochemical polymerization were used as recognition elements of a piezomicrogravimetric chemosensor for determination of nicotine and its metabolite – cotinine under FIA conditions. Morphology as well as spectral and electrochemical properties of the films was studied. Subsequently, the polymer films deposited on quartz crystal resonators were employed as recognition elements of a piezomicrogravimetric chemosensor for determination of nicotine and cotinine. Spectral results indicated that the porphyrin macrocycles remain essentially intact during electropolymerization for both porphyrin monomers used, which is a prerequisite for successful polymer application as the recognition element in the chemosensor. AFM imaging as well as spectral and electrochemical studies point to differences in morphology, porosity and cross-linking between polymer films formed from the monomer bearing two and one acetamide arm. More open structure of the former polymer film was also reflected by higher sensitivity towards nicotine as compared to that of the chemosensor coated by the latter film. FIA studies of the (porphyrin polymer)-resonators allowed for determination of adsorption and desorption rate constants of the studied analytes in the polymers as well as stability constants of the (zinc porphyrin polymer)-analyte complexes. Analytical parameters of the newly devised chemosensor were also evaluated.

LUNCH

Saturday afternoon, 7 November, 13:00

Afternoon Session 1

Saturday afternoon, 7 November, 14:00

Chair: Brand, I. d'Souza, F.

14:00 Tutorial lecture

Nanostructured molecularly imprinted polymers - synthetic receptors for protein recognition

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Molecularly imprinted polymers (MIPs) are synthetic receptors that specifically recognise target molecules. MIPs have found applications for example as antibody mimics in immunoassays or as recognition elements in biosensors [1]. They are produced by polymerising interacting and cross-linking monomers in the presence of the target molecule that acts as a molecular template. Although the technique has been used preferentially with small targets of the size of an amino acid or a small peptide, proteins can also serve as templates. However, due to their size and the possibility of denaturation under the conditions normally used in molecular imprinting, specifically adapted protocols and materials have to be developed.

A possible approach is the synthesis of the MIP in the form of soluble, nanometer-sized microgels. In that case, statistically, the majority of the binding sites created in the particle will be accessible from the solution. We describe here a new strategy for the synthesis of such materials by generating a three-dimensional image of the region at and around the substrate binding site of a model protein, the enzyme trypsin. The polymerisation is conducted with a specific monomer carrying the trypsin-inhibitor benzamidine. The growing polymer chain is thus confined to the substrate binding site of the enzyme, while the imprinted network is obtained by adding hydrophilic co-monomers. All imprinted polymers exhibit a much higher affinity towards the enzyme than the chemically identical non-imprinted control polymers (NIPs). We were able to demonstrate competitive inhibition of trypsin by the MIP with an inhibition constant of K_i= 79 nM, almost three orders of magnitude was stronger than that of free 4-aminobenzamidine (K_i=18.4 µM) [2].

Another approach is to create imprints of the protein in a thin film deposited on a surface. Here we describe the preparation of a MIP for cytochrome c. We use, for the first time, chemical force spectroscopy for the direct detection of molecularly imprinted binding sites. In order to obtain accessible surface binding sites, we chemically immobilised the template protein onto a flat surface before imprinting. The MIP was then cast on that surface and was bonded onto a glass support. After removal of the template protein, the MIP was tested for selective binding of cytochrome c by fluorescence measurements with FITC-labelled cytochrome c. Other proteins and a non-imprinted polymer surface were used as controls. At the nanometric scale, AFM and molecular force spectroscopy were employed to directly reveal molecularly imprinted binding sites. For the latter, AFM tips were modified with cyt c and used to evaluate the affinity of the MIP for the target protein. Control experiments with other proteins were performed to confirm the existence of specific binding sites [3].

As an extension of this approach, the MIPs can be synthesised in the form of surface-bound nanofilaments with a high aspect ratio. This results in an increase in surface area and thus the number of accessible binding sites, which is particularly important for the use of the MIP in a biosensor. This can be achieved by nanomoulding the polymer on a porous starting material like anodised alumina. The target protein was first coupled to the alumina, and the polymer was then cast on that surface. After chemical dissolution of the alumina, polymer nanofilaments were obtained with surface molecular imprints. The number and size of the nanostructures could be fine-tuned by adjusting the morphology of the initial template surface. The molecular imprinting effect was demonstrated using the FITC-labelled protein. By patterning the MIP surface using projection photolithography, arrays of nanostructured dots were obtained that can be used in biochips [4].

In order to increase the sensitivity of detection with MIP-based sensing systems, we have explored the possibility of using nanocomposites of MIPs and metal nanostructures. We have found that Raman spectroscopy and surface-enhanced Raman scattering (SERS) measurements were possible on single MIP nanostructures [5].

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14:40 Keynote lecture

Dynamics of electrochemical bond cleavage in immobilised reagents

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The principles of dissociative electron transfer applied to the specific case of surface-attached reagents are first reviewed, and explored for the case of an experimental system. The utility of these techniques for the formation of stable, surface-attached ferrocene systems will be covered.

15:00 Short communication

An effective multipurpose building block for 3D electropolymerizations: 2,2'-bis(2,2'-bithiophene-5-yl)-3,3'-bi-1-benzothiophene

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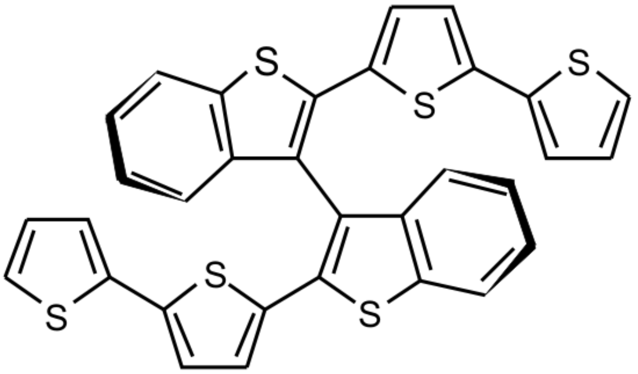

Thiophene-based oligomers are a boundless class of organic semiconductors and starting materials for the preparation of electroactive films. Current molecular design strategies in this field address a trade off between two key requirements: branching, to achieve the required solubility for industrial processing, and planarity, to achieve the highest possible conjugation efficiency. In particular, our recent investigations on spider-like oligothiophenes[1,2] have shown that the electronic properties of these molecules do not depend on the overall number of thiophene moieties but on the number of (i) conjugated thiophene moieties in the longest α,α'-linked chain and (ii) "*nodes*", i.e. distorsions from planarity, along the same chain.

In most cases, the presence of *nodes* is regarded as an undesirable feature, reducing the effective conjugation length. However, the intrinsic 3D character of the *nodes* can be useful when employing these molecules as starting compounds for electropolymerization.

A good example is provided by our 2,2'-bis(2,2'-bithiophene-5-yl)-3,3'-bi-1-benzothiophene (shown in Figure). It consists of two identical, approximately planar moieties, each having one terminal α thiophene position available for polymerization, with a central *node*. From the electroche-mical point of view, this structure implies the presence of two equal, slightly interacting conjugated systems, each one being approximately equivalent to a α-terthiophene. Calculations have shown the central *node* corresponds to a 70° angle and the energy barrier sufficiently high to yield two stable enantiomers, an attractive feature in the perspective of obtaining optically active conducting films devoid of stereocenters.

Consistently with its intrinsic 3D nature, this molecule electropolymerizes very rapidly and regularly, a behaviour steadily maintained even after many cycles. This feature can be advantageously exploited to promote 3D copolymerization with monomers having useful functional properties, but being intrinsically able to yield only 2D films. Several examples will be presented, including the preparation of a melamine-templated molecularly imprinted polymer (MIP) film yielding very good performance as a recognition element of a selective piezomicrogravimetric chemosensor.[3]

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15:15 Short communication

A melamine acoustic chemosensor based on molecularly imprinted polymer film

Agnieszka Pietrzyk[1], Wlodzimierz Kutner[1], Raghu Chitta[2], Melvin E. Zandler[2], Francis D'Souza[2], Francesco Sannicolò[4], Patrizia R. Mussini[3]

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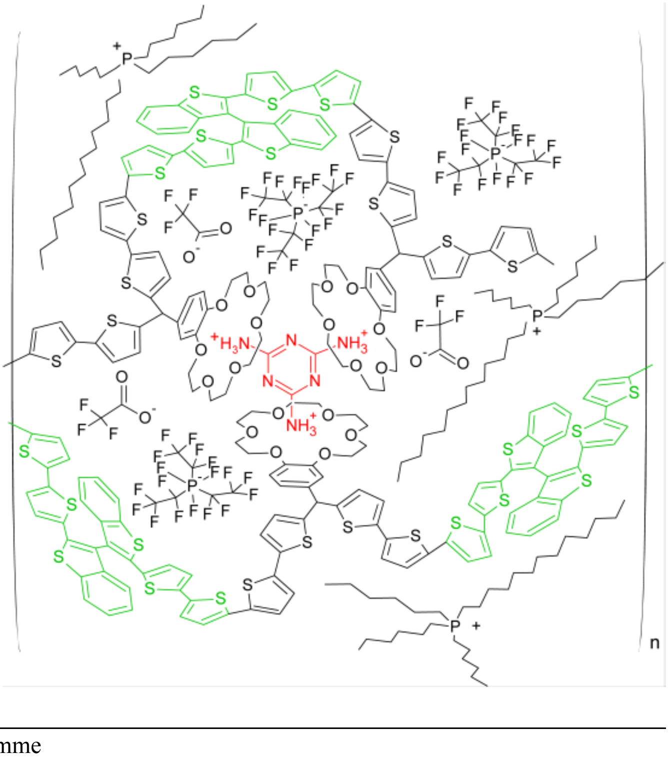
A melamine piezomicrogravimetric (acoustic) chemosensor using a molecularly imprinted polymer (MIP) film was devised and tested. A melamine-templated MIP film and a 10 MHz AT cut shear thickness mode bulk acoustic wave quartz crystal resonator with Pt film electrodes served as the recognition element and signal transducer of the chemosensor, respectively. The MIP films were prepared by electrochemical polymerization, performed under simultaneous cyclic voltammetry (CV) and piezoelectric microgravimetry (PM) conditions, using an electrochemical quartz crystal microbalance (EQCM), on the Pt/quartz resonator substrates. For MIP preparation, the melamine template was first complexed in solution by a functional monomer of the bis(bithiophene) derivative bearing an 18 crown 6 substituent, at the monomer to template mole ratio of 3 : 1, and then electrochemically polymerized. The structure of the MIP-melamine complex was visualized by DFT B3LYP/3-21G(*) energy optimization calculations. Sensitivity and selectivity of the MIP film was largely increased if the polymer was crosslinked with bithianaphthene monomer. Moreover, the presence of an ionic liquid, used as a porogenic solvent of the pre polymerization solution, additionally enhanced sensitivity of the chemosensor. The ionic liquid played also a role of the supporting electrolyte in the electropolymerization. After electropolymerization, the melamine template was extracted by soaking the MIP film in an aqueous strong base solution. The UV-vis spectroscopy, XPS, and electrochemical measurements confirmed extraction of the melamine template from the MIP film. Additionally, the SECM imaging bore out removal of the melamine template from the MIP film and then rebinding of the melamine analyte. The AFM and SEM imaging emphasized relative roughness and porosity, respectively, of the MIP films. The analytical as well as some kinetic and thermodynamic parameters of the chemosensing were assessed under flow injection analysis (FIA) conditions with PM detection. The melamine dynamic concentration range was at least 5 nM to 1 mM. The lower concentration limit of detection was as low as ~5 nM melamine. The chemosensor was selective with respect to common interferants, such as cyanuric acid, cyromazine, and ammeline.



Scheme. Excerpt of structural formula of the MIP-melamine film.

COFFEE

Saturday afternoon, 7 November, 15:30

Afternoon Session 2

Saturday afternoon, 7 November, 15:55
Chair: Baker, P.G. Millner, P.A.

15:55 Keynote lecture

Electrochemical Communication between Viable Bacterial Cells and Flexible Redox Polymers

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During the last few years we have proven that viable bacterial cells can be electrochemically ”wired” to electrodes with flexible $Os^{2+/3+}$ functionalised polymers such as poly(1-vinylimidazole)$_{12}$-[Os(4,4’-dimethyl-2,2’-dipyridyl)$_2$Cl$_2$]$^{2+/3+}$ and poly(vinylpyridine) [Os(N,N’-dimethyl-2,2’-biimidazole)$_3$]$^{2+/3+}$. Our initial studies[1] in this field were made with the structurally rather simple gram-negative *Gluconobacter oxydans*, where we addressed redox enzymes from the cytoplasmic membrane yielding response for glucose, fructose, ethanol and glycerol. In further studies focus was on the structurally more complex gram-negative *Pseudomonas putida* and *Pseudomonas fluorescens*,[2,3] where response currents could be obtained both for substrates being metabolised in the cytoplasmic membrane (glucose) as well as in the cytosol of the cell (phenol). Recently we have also showed that introduction of a cytochrome to the cytoplasmic membrane of *E. coli* greatly facilitated the communication between these gram-negative bacterial cells and the osmium polymers.[4] In the current study reported here[5], we now use the gram-positive model organism *B. subtilis*, with a substantially thicker peptidoglycan cell wall, which at an early glance is expected to be more difficult to permeate by the osmium polymeric mediators. In *B. subtilis* the cell wall has a diameter of ≈35 nm. It constitutes a multilayered structure composed mainly of peptidoglycan and teichoic acids. The polyelectrolytic properties of the peptidoglycan and teichoic acids provide a continuum of anionic charge between the cytoplasmic membrane and the environment. These properties of the cell wall may facilitate the connection between the cells and the polycationic Os-polymer and further to the electrode. Using a *B. subtilis* strain which overproduces succinate:quinone oxidoreductase (respiratory complex II), we were able to improve the current response several fold using succinate as substrate. We believe that the approach taken in this work adds to the understanding of how gram-positive cells may communicate with their surroundings through electron conductive structures present in the layers of peptidoglycan/ teichoic acids. This is also in line with the recent hypothesis raised by Ehrlich[6] on that electron conducting structures are present in the periplasm of gram-positive bacteria (peptidoglycan, teichoic acids), which must be responsible for conveying electrons from the cytoplasmic membrane to the outer surface of the cell wall. Another recent publication that support such a theory is the work by Marshall and May[7], who show that gram-positive *Thermincola ferriacetica* strain Z-0001 readily can grow onto a graphite electrode and exhibit direct electron transfer communication.

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16:15 Keynote lecture

Enzymatic fuel cells

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Biological fuel cells (biofuel cells) are fuel cells based on biocatalysts to transform energy of chemical compounds into electrical energy via redox reactions. In enzymatic fuel cells (EFC) both anodic and cathodic biocatalysts are redox enzymes. During the presentation general principles of EFC function will be shown, possible limiting steps of their performances will be discussed, and already existing devices will be presented.

Since 1969 substantial efforts were devoted to miniaturized implantable enzyme-based BFC for powering microscale medical biodevices. In spite of obvious advantages of glucose/oxygen EFC based on direct electron transfer (DET) reactions as power source for implantable devices (simple construction, ability for significant miniaturization, and less-toxicity due to the absence of redox mediators), there is only a limited number of reports describing membrane-, mediator-, cofactor-less DET-based EFC operating in physiological liquids of different compositions and pH values, e.g., blood, plasma, serum, saliva, and sweat. Already achieved parameters of glucose/oxygen DET-based BFC will be presented and possibility for their improvement will be highlighted. Moreover, possible applications of BFC in short- and long-term perspectives will be discussed.

Acknowledgements The work was financially supported by the Swedish Research Council and FP7 EU project NMP4-SL-2009-229255.

16:35 Short communication

Carbon nanotube nanostructured electrodes for membrane – less biofuel cell based on liquid-crystalline phases as matrices for enzymes

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The designed carbon bioelectrodes are based on the application of nanotubes with covalently bound ferrocene and ABTS as the anode and cathode mediators, respectively. Covalent binding to nanotubes allowed to eliminate leaching of the mediator to the solution – a difficulty often reported for soluble or adsorbed mediators. Laccase and glucose oxidase used as the biocatalysts were placed in lipid liquid crystalline film covering the electrode nanostructured with single-wall carbon nanotubes. The catalytic current of glucose oxidation was $1mA/cm^2$ and oxygen reduction current exceeded $0.6mA/cm^2$. The power output of the constructed biofuel cell was $100\mu W/cm^2$ without stirring of the solution. Further improvement in the power output and stability of the biofuel cell requires work on enhancing the supply of oxygen to the electrode and searching of enzymes not requiring mediating units other than carbon nanotubes.

16:50 Short communication

Pyrene functionalised single-walled carbon nanotubes for bioelectrocatalysis

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Recently it was shown that single-walled carbon nanotubes(SWCNTs) is a suitable support for non-mediated bioelectrocatalytic dioxygen reduction using the enzyme laccase. Further, it was revealed that the use of SWCNTs non-covalently functionalised with pyrene sulfonic acid through π-electron stacking significantly enhances the catalytic activity of the electrode. [1] However, the mechanism behind this enhancement is still not elusidated. Since similarly high catalytic currents were measured using electrodes modified with sulfonated carbon nanoparticles [2], as well as with nafion on multi-walled carbon nanotubes [3] it is suspected that the sulphor groups might be significant for the process.

In this communication we have investigated the electrocatalytic effect of SWCNT-supported laccase, where the SWCNTs have been functionalised with different pyrene compounds. The results are discussed in the light of trying to reveal important parameters for the direct electron transfer.

This research was partially supported by the European Union within the European Regional Development Fund, through Grant Innovative Economy (POIG.01.01.02-00-008/08).

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17:05 Short communication

Bilirubin oxidase modified carbon ceramic electrode for bioelectrocatalytic reduction of dioxygen supplied from gas phase

Wojciech Nogala[1], Anna Celebańska[1], Gunther Wittstock[2], Marcin Opallo[1]

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Enzyme modified electrodes for dioxygen reduction are often employed as cathodes in biofuel cells [1]. Some concepts of biofuel cells (BFC) involve anode modified with glucose oxidase. This enzyme is not specific for glucose electrooxidation, but dioxygen acts also as a substrate. Direct enzymatic oxidation of glucose by dioxygen is a side effect for bioanode, so there is current interest to apply dioxygen-free anodic compartment in BFC. On the other side, splitting of common electrolyte to two electrodes compartments using membrane and device-case causes increase of BFC size and cost of it. Gas phase biocathode made of porous material has already been poroposed [2].

In this work we employed carbon ceramic electrode (CCE) [3] modified with bilirubin oxidase for bioelectroreduction of dioxygen with use of deaerated electrolyte. Voltametric examnation was performed with different dioxygen partial pressures exerted on back side of this composite electrode. Dioxygen transport in porous, hydrophobic silicate (component of CCE) was examined using generation-collection mode scanning electrochemical microscopy [4].

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17:20 Short communication

The influence of some structural parameters on the performance of an enzymatic anode for glucose oxidation

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Enzymatic glucose-oxygen biofuel cells are possible alternative to conventional lithium-ion batteries for powering of small-scale implantable devices. Though, the implantable biofuel cell has to meet special demands due to its quite specific potential application. The enzymatic anode for such a cell has to fulfill several requirements including low oxidation overpotential, high current densities, sufficient oxygen tolerance and high long-term stability.

An immobilisation procedure employing conductive polypyrrole layer, a charge-transfer complex (CTC), Glucose oxidase (GOx) and a gelatin membrane has been developed. The influence of different parameters, including CTC loading and morphology, GOx loading, membrane thickness, etc. on the activity of the resulting bioanode has been investigated.

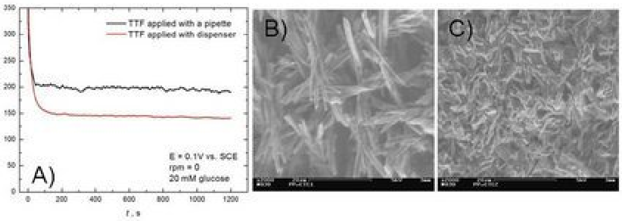

Figure 1: The influence of the CTC morphology on the glucose oxidation activity. A) Chronoamperograms of the different anodes in presence of glucose; SEM images of CTC when TTF solution was applied with B) pipette and C) dispensing robot.

17:35 Short communication

Poly-o-aminophenol as laccase mediator and influence of enzyme on the polymer electrodeposition

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Applicability of poly-o-aminophenol (POAP) as redox mediator for fungal laccase is investigated and compared with other conducting polymer matrices. Laccase has been entrapped by means of electrochemical polymerization carried out in the solution containing monomer and enzyme. The obtained layers have been characterized by cyclic voltammetry in deaerated and oxygen saturated solutions, as well as by spectroscopic methods. The activity of enzyme has been verified by the standard test using syringaldazine.

Laccase immobilized in POAP matrix catalyses oxygen reduction without any additional mediators. POAP is able to mediate the electron transfer between the enzyme active site and the electrode surface similarly to poly-o-phenylenediamine which has been studied previously [1]. Similar electrocatalytic currents are observed, but the oxygen reduction potential is shifted by as much 0.4 V towards positive direction making POAP the promising candidate for application as material for bio-fuel cell cathodes.

The role of laccase in electrodeposition of POAP has been explored. It was found that the polymer layers obtained during the enzyme entrapment procedure are significantly thicker comparing to POAP layers obtained in absence of enzyme. Furthermore, laccase facilitates formation of longer polymer chains as revealed by UV/VIS absorption spectra. Raman experiments indicate that molecular structures of POAP layers electrodeposited with and without enzyme are similar.

The monomer belongs to typical laccase substrates. Addition of laccase to the o-aminophenol solution causes immediate formation of brownish soluble oligomers. After few hours brown precipitate becomes visible. The precipitate is composed from long polymer chains as revealed by spectroscopic results. POAP formed by laccase contains nanostructures. Its morphology differs from typical polymer samples synthesized chemically or electrochemically. Consequently, application of laccase as polymerization initiator might be manner of controlling the morphology of polymer samples.

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17:50 Short communication

Surface Imprinted Micro- and Nanorod Polymers with Magnetic Cores for Protein Recognition

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The ability of molecularly imprinted polymers (MIPs) to selectively recognize (bind) target molecules, e.g., proteins, makes them analogous to receptors of biological origin. Compared to antibodies used for protein assays, MIPs can offer some advantages like the lower production cost and the better chemical and physical stability. The downside of protein imprinting is the large size of the proteins that prevent them to reach the active binding sites inside the polymer matrix. For this reason the usual bulk polymerization cannot be used. Instead we have used a novel nano-moulding approach.

In this method a sacrificial membrane with the template adsorbed on the surface of the micron sized through pores of the membrane is placed over a gold electrode and then conducting polymer rods of poly-3,4-ethylenedioxythiophene (PEDOT) were grown electrochemically into the pores. After the membrane dissolution and the template removal, MIP rods localized on the electrode are formed with a high concentration of active binding sites on their surface.

To increase the application range of these conducting polymers, we incorporate nanosized magnetic particles inside the rods, to obtain magnetic nanorods. With this approach the nanorods are removed from the electrode surface and they can be used directly in solution, where they may be simply collected by a magnet. These particles can be used as matrices for immunomagnetic separation and purification of biological targets as well as in magnetic ELISA assays.

DINNER

Saturday evening, 7 November, 18:30

POSTER-CONT

Saturday evening, 7 November, 19:30

Sunday, 8 November

Morning Session 1

Sunday morning, 8 November, 9:00
Chair: Wittstock, G. Wadhavan, J.

9:00 Tutorial lecture

Scanning electrochemical microscopy into the nanoscale

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Scanning electrochemical microscopy (SECM) has developed to a standard tool for investigating electrochemical and (bio)catalytic activities on surfaces. However, until now it was still difficult to reduce the size of the used microelectrodes and to scan a surface with resolution in the 10 to 100 nm range. However, this resolution will become more and more important for understanding processes at surfaces and elucidate local electrochemical activity. The tutorial lecture will give an introduction into SECM and will describe the challenges to extend its application into the nm range.

9:40 Keynote lecture

Development of novel bioelectrocatalytic systems through controlled combination of multiwalled carbon nanotubes, redox mediators and enzymes

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Recently, multi-walled carbon nanotubes (MCNT) have gained considerable attention, because of their remarkable electronic and mechanical properties, which have made them extremely attractive for a wide range of sensing applications from structural materials to nanoelectronic components. The ability of MCNT modified electrodes to promote electron transfer reactions has been documented in connection with important biomolecules [1]. Our goal is to explore new applications of MCNT as a electrode material in facilitating the electron transfer between biomolecules and electrode in bioelectrocatalytic systems of potential utility for biofuel cells.

This lecture will give an overview and discuss anode and cathode reactions based on multi-component films for oxygen and hydrogen peroxide reduction and fuel oxidation. Cathode reactions will cover those based on Co-porphyrin centers that are expected to induce reduction of oxygen at the initial stage, and the enzyme (horseradish or cabbage peroxidase) that should act as highly reactive catalyst capable of further reducing hydrogen peroxide intermediate [2]. The multi component bioelectrocatalytic film has also exhibited relatively higher activity towards reduction of hydrogen peroxide. Anode reactions will cover those based on mediated electron transfer. The presence of mediator is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode.

We have also considered utilizing new enzymes to design, characterize and evaluate different types and distinct configurations of enzyme-based multi-component and well organized bioelectrocatalytic systems capable of effective oxidation of ethanol in neutral media. At all stages of investigations, comparison have been made to the behavior (under analogous conditions) of glucose with glucose oxidase as model enzyme [3]. A special attention have been paid to development of mediation and enzyme immobilization methodology for continuous and efficient electron transfer from the enzyme to the electrode surface.

On the whole, a stable multifunctional composite bioelectrocatalytic films for fuel oxidation and oxygen reduction under neutral conditions are produced. Finally, the formation, morphology, structural transformations and electrochemical properties of the MCNT-containing three-dimensional network films have been examined using cyclic voltammetry, potential step techniques, rotating disc voltammetry, FTIR spectroscopy and tranmission electron microscopy. The ability to create bioelectrocatalytic nanocomposites provides an opportunity to construct functional bioanodes and biocathodes. Follow on research will use the approach to design a biofuel cell system that utilizes an nanostructured enzyme-based anode and cathode working in tandem.

References:

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10:00 Short communication

Horse-radish peroxidase-modified 3D-hierarchical carbon nanotube electrode - characteristics and potential applications

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The properties of biosensors or enzyme biofuel cells are unequivocally influenced by intrinsic characteristics of the used biological recognition element, such as the kinetics of the biocatalytic reaction, the presence of activators/inhibitors, etc. However, apart from these primary considerations which might be improved by screening of a large number of specific biological sources or through dedicated genetic modifications, the design of an intimate electronic communication and the robust fixation of redox enzymes at the electrode interface are crucial for benefiting of any particular characteristics of the biological element.

We have followed several directions for studying and designing new bioelectrochemical interfaces. Key parameters such as mass transport, optimum loading with the chosen enzyme, 3D design of the electrode area as well as maintaining efficient electronic conductivity for the entire 3D electrode surface were investigated at modified graphite electrodes [1]. Hence, such materials are considered promising for improving the performances of a bi-enzymatic membraneless biofuel cell [2].

Recently, new composite materials consisting of double-anchored carbon microfibers (CF) decorated either with carbon-nanotubes (CNT) or carbon-nanoballs demonstrate potential application as biocathode, by their modification with horse-radish peroxidase (HRP), as demonstrated by specific properties for reduction of H_2O_2, as it was previously observed also for micro-peroxidase [3]. One more time, these experimental observations clearly emphasize the still-not-fully-explored potential by which nanomaterials might contribute to expanding novel properties and characteristics of certain biological elements.

Dedicated applications of the present electrode architecture will be discussed.

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10:15 Short communication

Electrodeposition of metalloporphyrines for the preparation of electrocatalytically active surfaces

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PEM fuel cells (PEM: proton exchange membrane) are since long discussed as alternative energy-supplying system for e.g. household or mobile application. The commercialisation of PEM fuel cells, however, is strongly impeded by the high costs of the electrocatalysts, which mainly consist of carbon supported platinum and its alloys. Thus, cheaper alternatives are under investigation, one of them is carbon materials modified with metal-nitrogen centres, where the metal usually is iron or cobalt. These materials have initially been derived from metalloporphyrines or -phthalocyanines, which exhibit high activity for the oxygen reduction reaction (which constitutes the cathode reaction in fuel cells), albeit with low stability. The stability of these materials can be enhanced, when they are deposited onto carbon black and subjected to a heat treatment step.

Another important issue in current fuel cell research is the utilization of the catalysts within the gas diffusion electrodes needed to obtain high current densities during application. To prepare these, the catalysts are processed in form of a slurry containing additives, which is then sprayed onto a gas diffusion layer (e.g. carbon cloth) or the electrolyte membrane. An alternative to this approach would be, if firstly the gas diffusion electrode is prepared without the active material, and the latter would then be deposited onto this gas diffusion electrode. The advantage here is that the active material will only be deposited at sites which are electrochemically connected and will later participate in the respective electrocatalytic reaction, thus saving costly material.

Having this in mind, we are currently investigating techniques to electrodeposit metalloporphyrines onto carbon-based electrode materials. The employed porphyrines contain Fe, Co or Mn as central metal ions and are deposited via a pulsed potential technique. Substrates include flat glassy carbon surfaces but also layers of CNTs. CNTs have been chosen since they chemically much more stable then the usually employed carbon blacks, which tend to corrode under the conditions of a working fuel cell. Activity for the oxygen reduction reaction is determined by cyclic voltammetry and rotating disc electrode measurements; further characterisation includes e.g. SEM and XPS. It will be shown that electrodeposition of metalloprophyrines onto CNTs enhances their catalytic activity for the oxygen reduction reaction. Furthermore, activity is strongly influenced by the substituents at the macrocyclic ring as well as the nature of the central metal ion, with Mn porphyrines exhibiting activity similar to that of the more frequently used iron porphyrines. Heat treatment of metalloporphyrines when deposited onto CNTs enhances their activity with the optimum heat treatment temperature being in the range of 650 - 850 °C.

COFFEE

Sunday morning, 8 November, 10:30

LECTURE

Morning Session 2

Sunday morning, 8 November, 10:55

Chair: Hamou, F.R. Boukherroub, R.

10:55 Keynote lecture

Generator/collector experiments at a single, chemically-modified electrode: introduction and general applicability

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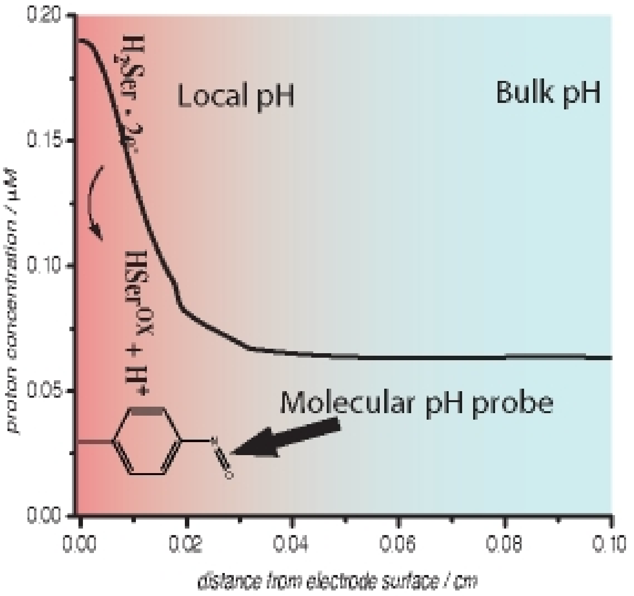

We demonstrate proof-of-concept that generator-collector experiments can be performed at a *single* macroelectrode and used to determine mechanistic information. The facile chemical modification of a graphite electrode with pH sensitive redox active molecules results in the formation of a *single* electrode generator/collector electrode system. Using the oxidation of serotonin as a model system, we demonstrate that the *single* generator/collector electrode is capable of measuring changes in *local* pH immediately adjacent to the electrode surface, i.e. within the diffusion layer, during the oxidation process. Comparison of experimental data with simple 1-D numerical simulations was used to ascertain that the serotonin oxidation mechanism in poorly buffered media initially involves the transfer of two-electrons and only one proton, in an ECE mechanism. This approach compares favorably in terms of sensitivity to traditional double electrode experiments such as the use of rotating ring-disc electrodes.

Experiments were also performed with a different molecular pH probe, either dissolved in the electrolyte solution or attached to the electrode surface, in order to compare the general feasibility of this approach. The reduction of dissolved oxygen in water was used as a model system with which to compare the performance of the two approaches. The results of these experiments suggest that the single-electrode generator/collector approach is potentially readily applicable to a much wider range of electrochemical systems.

11:15 Keynote lecture

Silica-based mesoporous materials in electroanalysis: interests and limitations

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Silica-based organic-inorganic hybrid materials have become increasingly attractive for analytical and electroanalytical purposes by exploiting their advanced properties in aqueous suspensions or at an electrode/solution interface.[1,2] In particular, those materials displaying a regular structure at the mesoporous level have been found to be very promising electrode modifiers because they ensure fast mass transport processes, which are often rate-determining in electrochemistry.[3,4] The aim of this lecture is to highlight and discuss some recent achievements performed with using such new materials in electroanalytical chemistry, especially by pointing out their advantages but also their limitations.

After a brief overview of the actual developments in this field, special attention will be given to two particular examples: (1) Hg^{II} preconcentration on mesoporous silica samples functionalized with thiol groups, and (2) Cu^{II} binding to amine-functionalized materials. The first example will demonstrate the definite advantage of mesostructured organically-modified silicas over their non-ordered homologues, as a result of better accessibility to the binding sites and faster transport of the analyte because of unrestricted diffusion.[5,6] This can be exploited for the voltammetric detection of Hg^{II} species, in the anodic stripping mode subsequent to open-circuit accumulation. The second example will point out some problems related to the poor chemical stability of silica adsorbents bearing alkaline functional groups (i.e., amine-containing ones)[7] and will discuss some strategies to overcome such limitations by the resort to polyazamacrocycles attached to the silica surface via 1, 2, or 4 alkyl arms.[8,9]

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11:35 Short communication

A facile preparation of the nanoparticulate film from conductive and nonconductive particles of the opposite charge

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Layer by layer deposition strategy is well known and broadly applied [1-5]. The most popular approaches are alternating deposition of the oppositely charged organic polyelectrolytes [1, 2] or alternating deposition of polyelectrolyte and charged particles [3-5]. Only few experimets where LbL film was obtained by alternating deposition of the oppositely charged particles are known [6, 7]. According to our knowledge there are no reports on LbL conductive film composed with conductive and nonconductive particles mixture.

The new LbL modified electrode was designed. ITO covered glass substrate was subsequently modified with the positively charged covalently bonded ionic liquid mesoporous silicate submicroparticles [8] and negatively charged sulfonated carbon nanoparticles.

Electrochemical properties of the new modified electrode were investigated. It was found that new electrode shows accumulation properties towards ABTS. Nearly no accumulation was visible in the case of $K_4Fe(CN)_6$. One can conclude that ABTS adsorption is caused rather by the presence of carbon particles than electrostatic interactions.

Electrochemicaly active surface development was shown with H_2O_2 electroreduction.

The electrode exhibits electrocatalytic properties towards NADH oxidation. New electrode has been also found as a promising support for enzyme immobilization. After laccase adsorption electrode exhibits mediatorless bioelectrocatalysis of dioxygen reduction.

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11:50 Short communication

Conduction in Nanoparticle Assemblies and Mesoporous Films

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The assembly of nanoparticle building blocks and suitable binders provides a versatile approach for functionalising electrode surfaces with porous and/or functional structures. Examples of structures include TiO_2-based films [1], Fe_2O_3-based films [2], composite TiO_2-Au-based films [3], films incorporation SnO_2 nanoparticles [4], carbon nanoparticles [5], and purely organic structures based on reconstituted cellulose-nanofibrils [6]. In this presentation electrical conductivity in these types of nano-composite films will be surveyed and compared. Novel mechanisms based on surface processes and based on "Faradaic coupling" will be discussed.

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12:05 Short communication

Bioelectrocatalytic electrode obtained by layer-by-layer assembling of sol-gel processed ionic liquid and hydrophilic carbon nanoparticles and adsorbed bilirubine oxidase

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The layer by layer method [1] become important for preparation of bioelectrocatalytic electrode. However, only recently it was applied to obtain biocathodes potentially applicable in biofuel cell [2, 3]. Our group shown that the nanoparticulate film electrode prepared by layer by layer method combined with sol-gel process exhibits mediated bioelectrocatalysis with laccase dissolved in electrolyte. The electrode modified by film assembled from osmium redox polymer and laccase layers also catalyses dioxygen reduction .

Here we will show bioelectrocatalytic behaviour of earlier proposed electrodes modified with adsorbed bilirubin oxidase from Myrothecium sp. (EC 1.3.3.5). Clearly mediatorless bioelectrocatalysis indicates efficient electron exchange between the enzyme and carbon nanoparticles [4]. The catalytic current is significantly larger if mediator: 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) is preadsorbed at the electrode. One can conlude that in the latter case two processes mediated and mediatorless occurs simultaneously. The bioelectrocatalytic current is proportional to the number of immersion and withdrawal steps in electrode preparation procedure.

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12:20 Short communication

Ion Association Effects in Cellulose – Poly-(Diallyldimethylammonium) Reassembled Membranes Immersed in Acetonitrile

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Cellulose is one of the most abundant raw materials. It is an excellent natural absorbent and employed for many separation and chromatography applications. Natural celluloses can be digested into nanofibrillar cellulose and then re-assembled in to novel nanocomposites [1]. The versatility of cellulose and the facile incorporation of “receptor” components into nanocellulose films [2] are of interest in sensor development, membrane technology, and drug release applications. Ion association effects are commonly observed when cellulose-nanocomposite membranes are immersed in aqueous media [3]. In this study, the interaction of electro-generated ions is investigated with cellulose – poly-(diallyldimethylamonium) (PDDA) membranes immersed in acetonitrile.

Cellulose-PDDA film deposits are formed at glassy carbon electrode surfaces and the properties of these films (in terms of ion permeability, ion absorption, and specific binding) are investigated for two model redox systems in acetonitrile: (i) the reduction of duroquinone and (ii) the oxidation of ferrocene. The composition and thickness of the cellulose-PDDA film deposit are important in controlling the electrochemical behaviour. Anion binding for example for duroquinone radical anions is observed.

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Thielemans, F. Marken, J. Phys. Chem. C, 112 (2008) 2660.

12:35 Short communication

Interrogation of polyaniline-polystyrene nanocomposite as impedimetric platform for direct ochratoxin A immunosensor

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Ochratoxin A (OTA) is a mycotoxin produced as a fungal secondary metabolite by several *Aspergillus* and *Penicillium* species growing on stored and processed agricultural products. The toxin causes carcinogenic, tetratogenic, estrogenic, nephrotoxic and immunosuppressive health conditions in both humans and animals. In humans, the consumption of food contaminated by OTA has been indicated to cause Balkan endemic nephropathy, a disease characterised by severe kidney damage. Currently, HPLC coupled to a fluorescent detector is the preferred method for testing for OTA and its metabolites. Thin-layer and gas chromatographic techniques as well as enzyme-linked immunosorbent assay have also been used to determine OTA. These methods have excellent sensitivities and limits of detection but require extensive sample pre-treatment, skilled labour and expensive equipment. On the other hand, electrochemical immunosensors are easy to use, require very minimal sample pre-treatment and detect low concentrations of target antigen. In this study, a direct electrochemical immunosensor for the detection of OTA was developed. Ochratoxin A antibody was immobilised onto a glassy carbon electrode modified with polyaniline-polystyrene nanocomposite doped with a novel bis[N-(phenyl)3,5-di-tert-butylsalicyladiminato]-cobalt(II) complex. The biosensor’s ac and dc voltammetry characteristics were used to optimize the biosensor. Faradaic electrochemical impedance spectroscopy calibration of the nano-immunosensor responses was performed with aliquots of standard OTA solution in phosphate buffer (pH 7.2). Response profiles of the composite Ochratoxin A immunosensor include a detection limit of 80 µg/L and a sensitivity of 657 kW L/µg. The sensor was applied in the analysis of certified samples of maize meal, sorghum and poultry feed.

LUNCH

Sunday afternoon, 8 November, 13:00

Afternoon Session 1

Sunday afternoon, 8 November, 14:00
Chair: Kulesza, P. Gorton, L.

14:00 Tutorial lecture

Surface Molecular Assemblies Based on Surface Coordination Chemistry of Functional Metal Complexes Towards Molecular Devices

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Surface coordination chemistry has a promising potential to construct a well-defined surface functional architectures such as metal-organic framework and 2D layered structure on surface. In order to arrange the molecular units on the surface, surface anchors play an important role to determine the molecular orientation and the surface density of the molecules. Here, we present the fabrication and functions of surface molecular assemblies based on photo- and redox-active metal complexes with multipod anchors. Particularly, we discuss two topics as shown in Fig. 1; *i.e*, (1) dsDNA wires between two electrodes and (2) layered photoelectrochemical molecular devices with memory effect on a solid surface.1)

1) Fabrication of DNA wires by surface immobilized DNA intercalator:1) A novel Ru complex bearing both an acridine group and anchoring phosphonate groups was immobilized on a surface in order to capture double-stranded DNAs (dsDNAs) from solution. The immobilized surface could capture DNAs; however, the optimal number of molecular density on the surface exist to obtain the extended dsDNAs on the surface. The construction of DNA nanowires on the Au/SiO2 patterned surface was accomplished by the molecular combing method of the selective immobilized Ru complex on Au electrodes. These interconnected nanowires between Au electrodes were used as a scaffold for the modification of Pd nanoparticles on the DNA.

2) Combinatorial approach to redox-active layered Ru complexes bearing tetrapod anchors:2) New tetrapod phosphonate ligand XP and its Ru/Os complexes (Figure 1) have been synthesized. Oxidation potentials of [M(XP)(BL)M(XP)](M =Ru or Os) complexes on ITO electrode showed one-step two-electron process at +0.93 V for M = Ru and +0.66 V for M = Os, respectively. Layer-by-layer growth on ITO electrode was achieved by the surface assembling of the complexes with Zr(IV) ion. By changing the arranging order of the complex units with a variety of redox potentials, the different potential sequences were formed, some of which showed a current rectifier and a memory effect upon the photoelectrochemical response.

Fig. 1. Fabrication of multilayer and nanowire from molecular units with surface anchor group on surface.

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14:40 Keynote lecture

Application of DNA and RNA Beacons in Electroanalysis: What Are Limits for Sensitivity and Selectivity?

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At iNANO we aim at the development of new electrochemical biosensor technologies for analysis of cancer gene biomarkers, pathogens and small molecules of interest, which is crucial for efficient diagnostics of cancer and infectious diseases, and neurological disorders. We use small, functional DNA and RNA nanoblocks to create molecular assemblies with improved structural and biosensing properties that in combination with electrochemistry approach may provide extremely sensitive and accurate, yet simple, inexpensive and robust gene-based sensing platforms. I will overview the design and our studies of electrochemically-labeled DNA/RNA beacon structures that undergo distinct structural changes at electrodes upon hybridization phenomena (i.e. chemical recognition of one DNA sequence by another) or upon binding of other molecules of interest. In the latter case, we use so-called aptamers, which are nucleic acids designed to selectively bind to certain analyte, from small molecules to proteins and cells. I will discuss the general limits for selectivity and sensitivity of the developed assays.

15:00 Short communication

Electrochemistry of redox-labelled DNAs immobilized onto electrodes through the de-novo designed triazene linker

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Redox-labeled DNA was conjugated to and grafted to carbon and gold electrodes using the newly synthesized triazene linker. The chemical and electrochemical activation and deposition steps included using Me_2SO_4 reducing agent and further potentiostatically controlled deposition procedure. The produced DNA-modified electrodes exhibit remarkable DNA-hybridization properties which can be detected by a shift in the redox potential and they can easily be renewed by repeated hybridization/de-hybridization procedures. Electrochemical studies of surface coverage and DNA hybridization efficiency demonstrated that grafting through the triazene linker can successfully compete with existing protocols for DNA immobilization through the commonly used alkanthiol linkers and diazonium salts, while giving the practical advantage of one-step immobilization procedure.

15:15 Short communication

High-sensitive label-free detection of DNA hybridization based on intercalation

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Intercalation of small compounds into double stranded DNA (dsDNA) has been intensively studied during the past four decades due to the huge interest in the clinical use of compounds that bind strongly to DNA with applications as antitumor agents but as well as detection schemes for the quantification of DNA hybridization. Detection of hybridization events based on incorporation of suitable intercalating compounds into dsDNA may eliminate the need to modify the DNA target strand for further specific mo-dification reactions (e.g. introduction of covalently bound labels which is only possible during polymerase chain reaction (PCR)). Therefore, methods based on specific in-tercalation of suitable intercalators into dsDNA may simplify interrogation of DNA hybridization events.

Here, we present the effects caused by incorporation of Actinomycin D or profla-vine into dsDNA when interrogating the modified electrode surface with electro-chemical impedance spectroscopy (EIS). Intercalation is seen as an approach for avoiding any covalently bound labels. For this purpose, monolayers of thiol-modi-fied ssDNA were assembled on a gold electrode. The influence of the modified surface on the electron-transfer properties of negatively charged reversible redox mediators such as $[Fe(CN)_6]^{3-/4-}$ was investigated. Changes in physicochemical properties of the surface-assembled DNA upon hybridization and subsequently upon intercalation provoked significant changes in the charge-transfer resistance in EIS as elucidated by means of electrochemical impedance spectroscopy (EIS). These findings can be used as basis for the development of high-sensitive DNA assasy. The design of the sensing interface and the assay architecture will be presented. Moreover, a new strategy of hybri-dization signal amplification utilizing specifically modified intercalators will be dis-cussed. Enzymatic amplification for the high-sensitive detection of DNA sequences of multi-resistant germs such as Staphylococcus aureus (MRSA) using a 32 electrode microarray chip and parallel readout will be presented.

Acknowledgement Financial support by the European Commission in the framework of the project INTCHEM (MEST-CT-2005-020681) and by the Research School of the Ruhr-Universität-Bochum is acknowledged.

COFFEE

Sunday afternoon, 8 November, 15:30

Afternoon Session 2

Sunday afternoon, 8 November, 15:55

Chair: Shleev, S. Larbi, T.

15:55 Tutorial lecture

Electrochemical enzyme biosensors: from fundamental studies of the reactivity of enzymes immobilized on electrode surfaces to the elaboration of highly sensitive analytical devices

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The possibility to convert the catalytic activity of an enzyme immobilized on an electrode surface into an electric current has lead to the development of a wide range of electrochemical biosensors in various fields of analytical applications ranging from health to environment or food. It is possible to distinguished two main categories of electrochemical enzyme biosensors. The first one takes advantage of the electronic transduction of the catalytic and molecular recognition properties of an enzyme towards its substrate to provide an analytical means to detect the respective substrate. The most common approach used redox enzyme wherein the electron transfer between the electrode and the enzyme can be achieved with a small redox mediator that shuttles between the enzyme and the electrode or, less commonly, by direct electron transfer between the enzyme redox site and the electrode. A widespread example of such device is the commercialized blood glucose biosensor used by diabetes patients for monitoring their level of glucose in blood. The second type of electrochemical enzyme-based biosensors is related to the detection of the enzyme itself. This is typically the case in enzyme-amplified bioaffinity electrodes (as, for example, in electrochemical enzyme-amplified immuno- or DNA-sensors) that use the enzyme as an amplifying reporter label to achieve the electrochemical transduction of a biomolecular recognition event occurring between a target analyte molecule in solution and a receptor immobilized on the surface of an electrode. In this framework, enzyme labeling is thus a powerful manner of amplifying the electrochemical response. Coupling of several enzymes is also a promising way of boosting amplification. So far, most of electrochemical enzyme biosensors were however developed on an empirical base, where everyone offers his recipe for immobilizing the enzyme on the surface of an electrode, the final plots of the calibration curve serving to judge of the analytical performance of the device. The problem with this empirical approach is that it does not allow discerning the key factors that limit and govern the analytical performances of the biosensor, making it difficult to rationalize and optimize these devices. This is for this reason that, during the last years, our efforts have been directed towards the development of theoretical tools with the aim to predict the electrochemical current response (in particular, cyclic voltammetric responses) of the analytical device as a function of the mechanism and kinetics of the immobilized enzyme and the concentrations of species involved into the process, and with the aim to discern the key factors that limit and govern the analytical performances of the biosensor (1, 2). To achieve these goals, different enzymatic systems assembled as a mono-layer or multilayers on an electrode surface (using for example the avidin-biotin binding system) have been thoroughly investigated by cyclic voltammetry and analyzed with our theoretical kinetic models. Several of them will be presented with a particular attention to the specific case of enzyme-amplified bioaffinity electrodes (3).

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16:35 Keynote lecture

Label-free immunoassay based on functionalized nanopipettes

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Nanopipette technology is capable of detecting biomolecules based on difference on their size, shape and electrical charge. This unique label-free biosensor is inexpensive, easy to fabricate and versatile. It gives a fast and real time outuput even in small reactions volume (attoliters). At this point, the nanopipette size and geometry, together with the surface chemistry preparation for attachment of an antibody was optimized by both experiments and modeling to result in detectable signals by the nanopipette. In this phase, the goal of the surface chemistry procedure was to prepare nanopipette tip in a way that only controlled amount of the surface is functionalized and used for probe attachment. Preliminary experiments are demonstrating the sensitivity and selectivity of this technique with specific proteins targeting HPV as well as environmental toxins. These results prove that nanopipettes functionalized with apporporiate molecular recognition elements can be used as HPV/toxin sensors. A highly sensitive nanopipette probe can be precisely positioned, unlike other nanosensing technologies, at any subcellular region of a single living cell with submicron accuracy using a micromanipulator. This approach uses a movable sensor on an attached cell, in contrast to a fixed sensor detecting responses from floating cells. The functionalized nanopipette paves the way for in vivo immunoassay down to the single cell level.

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16:55 Keynote lecture

Soft interfaces for direct detection of biomolecules

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Attempts to get electrochemical responses towards small redox-inactive proteins are provided by analytical importance of these biological compounds. The common analysis either requires poisoning of animals or involves complicated and expensive technologies of molecular biology. Also great effort has been recently devoted to the new protocols development for the detection of DNA. Direct or label-free electrochemical detection of biomolecules is useful because it eliminates indicator addition/association/detection step and allows real time monitoring of binding.

Since water-soluble proteins and DNA molecules contain charged groups, and can even be considered as polyelectrolytes in aqueous solutions, it might be possible to detect them by means of electrochemical methods at soft interfaces either by changes of interfacial properties of supported layers of amphiphiles or by their transfer from water to organic phase or by bioaffinity interactions affecting the ion transfer through the interface.

The uniform bilayers of water-insoluble surfactants can be formed as a result of self-assembling at solid electrode support [1]. It was shown that bilayers are sensitive for binding events on the their surface and can be used as transducers for affinity interaction detection [2].

The novel system based on a hydrophobic electrode modified with thin liquid film of solution of water-insoluble redox probe in water-immiscible organic solvent was elaborated and applied for investigation of thermodynamics of ion transfer across liquid|liquid interface [3]. In contrast to the conventional four-electrode electrochemical setup [4], the potential window did not changed dramatically in the presence of surfactants in sufficient concentration. The redoxactivity of probe in organic phase was sufficiently enhanced after extraction of protein molecules into the thin film with the reversed micelles of surfactant AOT [5, 6]. Unlike the pure buffer the incubation in protein solution lead to the sufficient increase of currents of redox-activity of polymer, which in certain cases exceeds two orders of magnitude. Our studies gave strong evidence, that the raise in current at liquid|liquid interface is generated by the proteins. The mechanism of electrode process is elaborated. The peak current of electroactivity is dependent on the protein content in a wide concentration range, which gives promise for analytical applications of the system. The certain selectivity was achieved by electrochemical impedance spectroscopy.

In parallel route of research, it was suggested to use ion transfer at thin film electrodes modified with adsorbed oligonucleotides as an electrochemical probe for DNA hybridization. The setup based on ITIES supported by gel onto common disposable screen-printed electrode allowing thermodynamic controlled ion transfer was proposed. The ion transfer of organic cathions from organic into aqueous phase has been achieved in certain conditions. The adsorption of DNA probes onto ITIES was observed with electrochemistry.

The increase of conductivity has been observed in impedance spectra after hybridization [7]. The sensitivity of the system allowed determining the single mismatch in target sequence.

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17:15 Short communication

Triple Phase Boundary Photo-Voltammetry: Resolving Rhodamine B Reactivity in 4-(3-Phenylpropyl)-Pyridine Microdroplets

Andrew Collins[1], Xiaohang Zhang[1], Laurie M. Peter[1], Jonathon J. Scragg[1], Gary J. Blanchard[2], Frank Marken[1]

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The Rhodamine B base is employed as a redox system in a liquid|liquid electrochemical system. Microdroplets of 3-(4-phenylpropyl)-pyridine (PPP) containing Rhodamine B are deposited onto a basal plane pyrolytic graphite electrode surface which is then immersed into an aqueous solution containing 0.5 M pH=12 phosphate buffer solution. In cyclic voltammetry experiments conducted in the dark it is shown that reduction of Rhodamine B to leuco-Rhodamine occurs in two steps, both are one-electron processes, and re-oxidation occurs in a single two-electron process. For the first reduction, voltammetric signals are consistent with the Na^+ transfer coupled with the electron transfer, whilst for the second reduction the signals are consistent with a one-electron one-proton transfer. A chemical step occurs in the form of a proton driven disproportionation for the one-electron reduced species. This process has been shown to have a $k_{dis} = 3\ mol^{-1}\ dm^{-3}\ s^{-1}$.

The presence of light facilitates a photocatalytic oxidation process which occurs in place of the two-electron oxidation observed in the dark scans. A conproportionation is triggered by the photo-activation of Rhodamine B, (k_{con} = 0.7/[Rhodamine B*] s^{-1} at pH=12 where [Rhodamine B*] denotes steady-state concentration of the photoexcited state). Quantitative insights into the dark and photo-mechanisms are obtained by comparison behaviour of Rhodamine B and Rhodamine B octadecylester and by applying numerical simulation using DigiSim.

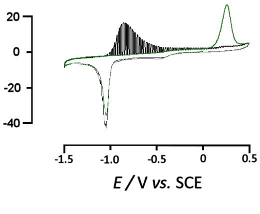

Figure 1. Comparison of the photocatalysed oxidation (black) and dark (green) voltammogram for the Rhodamine B base at 0.01 V/s^{-1}; 16 nl deposit, 0.28 M (Rhodamine B : PPP).

17:30 Short communication

Electrosynthesis of Ionic Liquid Covalently Bounded to Mesoporous Silicate at a Three Phase Junction Electrode|Liquid|Liquid

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Silica based sol-gel processed organic-inorganic hybrids are becoming important materials for electrochemical applications due to their easily tuneable properties like functionalisation, immobilisation and encapsulation as well as the different structures of these materials (film, particles, monoliths) [1]. They can be electrodeposited by electrochemical control of pH near the electrode|solution interface [2,3,4]. The generation of H_3O^+ ions – catalyst of the sol-gel process results in silicate film formation on the electrode surface. Recently, we proposed a three phase junction electrode|organic solvent|aqueous solution for silicate electrodeposition [5]. The electrode is immersed into a container with two immiscible liquids. The organic (unsupported) phase contains the precursor of the sol-gel process. Electrochemical generation of catalyst (H_3O^+) in the aqueous phase causes hydrolysis of the precursor near the three phase junction and a silicate stripe is formed [5]. It is also well-known that room temperature ionic liquids can be covalently bound to the organic-inorganic hybrids [6] to modify the electrode surfaces. In this communication a three phase junction microreactor is employed for electrochemically assisted sol-gel ionic liquid appended to mesoporous silicate material strip deposition. The factors affecting preparation and properties of the sol-gel processed materials is presented. The method seems to be compatible with controlled and localised deposition on heterogeneous supports, opening the way to electrochemically driven nanolithography [7]. Accumulation of electroactive anions into a silicate with covalently bonded room temperature ionic liquid strips deposited on an indium tin oxide electrode was studied. The effect was compared with an electrode modified with thin film of confined and an unconfined room temperature ionic liquid.

Acknowledgement Financial support from Ministry of Science and Education (research project N N204 054835) is gratefully acknowledged.

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17:45 Short communication

Carbon Dioxide Sensing Systems Based On Processes At Triple Phase Boundary Interfaces

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In this study, we developed a novel way to detect CO$_2$ based on ion transfer processes at a triple phase junction graphite|4-(3-phenylpropyl)pyridine|aqueous electrolyte. Cobalt phthalocyanine (CoPc) readily dissolved in the organic 4-(3-phenylpropyl)pyridine phase and exhibited oxidation/reduction processes which are coupled to liquid|liquid ion transfer. In order to maintain charge neutrality, each one-electron oxidation (reduction) process is coupled to the expulsion (insertion) of cations (here Li$^+$, Na$^+$, K$^+$, Ca^{2+} and Mg^{2+}). The introduction of CO$_2$ into the triple phase boundary system resulted in different potential shifts for all cation types studied. The range of cations studied allowed effects of cation sizes and CO$_2$ binding to the organic phase to be explored.

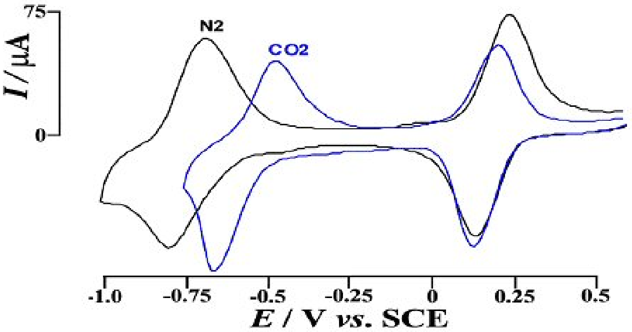

Figure. 1 Cyclic voltammogram at 0.05 V s^{-1} for the oxidation/reduction of 80 nL deposit of a solution of CoPc (84 mM) in 4-(3-phenylpropyl)pyridine, immobilized onto a 4.9 mm diameter basal plane pyrolytic graphite electrode, and immersed in 0.1 M NaClO$_4$, in the absence and presence of carbon dioxide.

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18:00 Short communication

Multistep electroreduction of fullerene C$_{60}$ in 1,2-dichlorobenzene-water biphasic system

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Ion transfer processes across an interface between two immiscible electrolyte solutions (ITIES) can serve as the basis for amperometric sensors, electro-assisted ion extraction, pharmacokinetics, electrocatalysis, etc. [1]. One of the methods to drive ions to transfer is to utilize the electrode reactions of a suitable redox probe present in one phase. Since the electroneutrality must be maintained in each phase, the electrochemical transformations are often coupled to ion transfer processes which can be detected electrochemically [2].

Fullerene C$_{60}$ is a suitable redox probe for studying ion transfer processes across ITIES since it can be reversibly reduced and its neutral and reduced forms are known to be practically insoluble in water. In our previous paper [3] we examined ion transfer processes coupled to the first electroreduction of fullerene and we reported anion-sensitive voltammetric response. Herein, we have extended our studies to the remaining two electroreductions and, to our best knowledge, this is the first time that the ion transfer processes accompanied to the consecutive three reductions of fullerene C$_{60}$ have been reported.

We have found that in the studied biphasic system comprising of 1,2-dichlorobenzene and water, fullerene C$_{60}$ undergoes three chemically reversible electroreductions which are accompanied to the expulsion of the anions of the supporting electrolyte which seems to act as an ion-exchanger. The calculated association constants show that the ion pair formation is thermodynamically more favored for more hydrophilic anions and this may stand for the observed ion-sensitivity. Moreover, the evolution of voltammograms shows that during electrochemical oxidations of fulleride species, the organic phase is progressively enriched with the aqueous anions that are preferentially associated with the tetrahexylammonium cations. Such a behavior provides the basis for ion detection whose sensitivity might be tailored by the choice of an appropriate tetraalkylammonium salt. To provide further insight into the mechanism of the overall process, the association between consecutive fulleride anions and tetrahexylammonium cations has been also examined.

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BANQUET

Sunday evening, 8 November, 19:00

Monday, 9 November

TRIP

Monday morning, 9 November, 9:00

LUNCH

Monday afternoon, 9 November, 13:00

Afternoon Session 1

Monday afternoon, 9 November, 14:00
Chair: Walcarius, A. Wilgoose, G.

14:00	Tutorial lecture

Immobilisation of proteins on biosensing surfaces using generic and specific affinity procedures

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Tethering of biomolecules to transducer surfaces (often but not exclusively proteins like enzymes and antibodies) represents a critical step in the fabrication of any biosensor where the aim is usually to achieve an optimum loading of the sensing molecule without compromising its biological activity. Initial procedures concentrated on chemical modification typically with reagents such as glutaraldehyde as amine to amine crosslinker, or the use of carbodiimide mediated peptide bond formation between surface carboxy groups and transducer amines (or vice versa). However, this often caused loss of activity and newer affinity methodologies represent a much cleaner and more targeted approach to biomolecule immobilisation.

Non-specific affinity procedures rely on the multi-point electrostatic interaction between antibody/enzyme and typically anionic polymer coated transducer surface. Biosensor fabrication is accomplished merely by dip coating the transducer into a solution of the protein and the procedure is very gentle and essentially irreversible. In addition, we have recently developed a procedure for simultaneous construction of a polyanionic surface and deposition of Prussian Blue mediator nanocrystals. There are also a wide range of specific affinity procedures. Tagging of the proteins with biotin allows cross linking with avidin to biotin tagged surfaces with very high efficiency and although the biomolecule must be chemically modified its activity can at least be checked prior to biosensor fabrication. Alternatively, polyhistidine tagged recombinant proteins, can be immobilised onto Ni^{2+} loaded NTA groups. This has the advantage that the transducer surface can be stripped of his_n - tagged protein using imidazole and reloaded with fresh sensing biomolecule. Finally, with antibodies (IgG), specific cleavage with 2-mercaptoethanolamine produces a "half-antibody" with unique cys groups on the Fc domain. The cys thiol then provides a unique target for the hetero-bifunctional crosslinker sulfoSMCC which has -NHS functionality for an amine loaded transducer surface, and maleimido functionality specific for the thiol groups, thereby allowing oriented attachment of the half antibody.

For both specific and non-specific approaches examples will be presented from our work on amperometric and impedimetric electrochemical biosensors and from nanoparticulate optical biosensor systems. I will also describe data using sugar binding biosensors that hint at the underlying mechanism of impedimetric biosensor operation.

14:40	Keynote lecture

Highly sensitive biosensors based on amorphous silicon-carbon alloys

Larbi Touahir[1], Anne Chantal Gouget-Laemmel[1], Philippe Allongue[1], Rabah Boukherroub[2,3], Jean-Nöel Chazalviel[1], Elisabeth Galopin[2,3], Catherine Henry de Villeneuve[1], Anne Moraillon[1], Joanna Niedziolka-Jönsson[2,3], Ionel Solomon[1], Sabine Szunerits[2,3], François Ozanam[1]

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Biosensors based on fluorescence and/or surface plasmon resonance (SPR) detection schemes are widely used owing to their ease of processing and good sensitivity. Their performance is frequently limited by the control of the surface chemistry. In this framework, the use of silicon substrates offers a promising alternative route for the grafting of functionalized organic monolayers through Si-C covalent bonding, providing robust immobilization chemistry. First, a carboxyl-terminated monolayer is grafted on hydrogenated surfaces via hydrosilylation. Then, the carboxyl groups are activated using NHS/EDC, followed by amidation with biological probes bearing a primary amine linker. By combining Atomic Force Microscopy (AFM) imaging and infrared quantitative spectroscopy, we have optimized these multi-step modifications.

To combine the advantages of well-controlled surface chemistry and sensitive detection, we have designed fluorescent and SPR biosensors based on a thin layer of hydrogenated amorphous silicon-carbon alloy (a-Si_xC_{1-x}:H) deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) on a metal layer. Chemical protocols developed on crystalline silicon surfaces were successfully transferred onto a-Si_xC_{1-x}:H. The sensitivity is maximized by optimization of the amorphous layer thickness and its carbon content. In this way, a fluorescence-based microarray on aluminium exhibits an efficient amplification of the fluorescent signal by over one order of magnitude as compared to commercial slides. Novel Au- or Ag-based sensitive plasmonic interfaces were also developed.

In either case, the obtained sensitivity allows for monitoring the hybridization of DNA probes with their complementary DNA in situ and in real time. Many successive hybridization/dehybridization cycles have been recorded without measurable changes in performance.

15:00 Short communication

Electron and Proton Transfer Across Biological Membranes, Measured Using Vesicles Immobilised on Electrode Surfaces.

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Immobilisation of redox proteins and enzymes on electrode surfaces forms the basis for the development of bionanotechnological systems and the use of electrochemical techniques provides opportunities to study their function in great detail. Membrane proteins and enzymes functioning as ion-channels or pumps regulate ion transport across cell membranes, a vital process for signal transduction and energetics of the cell. In particular redox enzymes, involved in cellular respiration utilise the free energy generated by electron transfer reactions to transport protons across membranes, generating a transmembrane proton electrochemical gradient used in cells for ATP synthesis. Although, such biomolecules can be difficult to manipulate, a membrane-friendly interface has been developed that allows the immobilisation of model membranes in the form of vesicles on Au electrodes. The pH-sensitive-fluorescent probe loaded vesicles remain intact on the SAM functionalised electrodes; and the incorporation of an ubiquinol oxidase, cytochrome bo_3 from *Escherichia coli*, allows studying the mechanism (proton pumping activity) of the enzyme, by monitoring the fluorescence response of the probe in real time. The activity of cytochrome bo_3 can be regulated by electrochemically tuning the redox state of ubiquinone that serves as an electron shuttle to the enzyme.

15:15 Short communication

Electrochemiluminescent biosensor for Palytoxin detection based on CNTs surface modifications.

Giovanni Valenti[1], Valeria A. Zamolo[2], Stefania Rapino[1], Alan Le Goff[2], Marco De Bortoli[2], Francesco Paolucci[1], Maurizio Prato[2], Massimo Marcaccio[1], Aurelia Tubaro[2]

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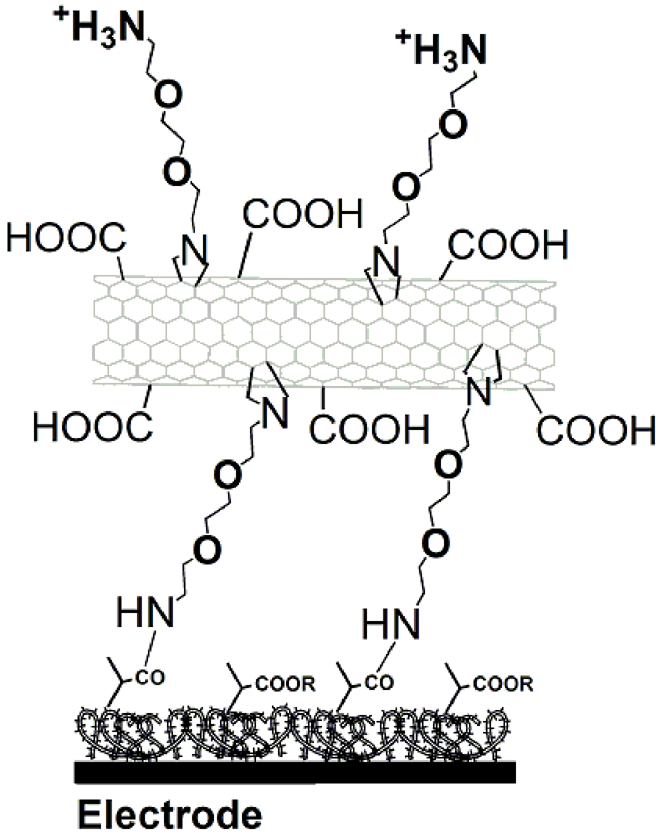
Electrogenerated Chemiluminescence (ECL) is a redox induced emission.[1] ECL is the processes whereby species generated at electrodes undergo high-energy electron transfer reaction to form excited states that emit light. Since its first application, the ECL technique, has become a very powerful analytical tool and has been widely used in biosensor transduction.[2] The ECL presents an intrinsically low noise and high sensitivity; moreover, the electrochemical generation of the excited state prevents scattering of the light source: for all these characteristics, ECL is an elective technique for ultrasensitive immunoassay detection. The majority of ECL systems involve species in solution where the emission occurs in the diffusion layer near to the electrode surface. Over the past few years, an intense research has been focused on the ECL generated from species constrained on the electrode surface. Nowadays, more and more attention has been paid to ECL biosensors functionalized with nanomaterials due to the combination of the unique physical and chemical proprieties of the nanomaterial with the excellent aforementioned properties of ECL. In this context, the composite materials based on carbon nanotubes (CNTs) are particularly promising for sensing applications. In fact, an improvement in sensitivity and stability of ECL biosensors was obtained from the modification of the electrode surface with CNTs. Moreover, proteins and enzymes can be easily immobilized within or on the CNTs either by physical adsorption or covalent binding, often involving the carboxylic functionalities introduced onto the CNT surface by oxidizing procedures.



In the present research we combined ECL transduction with the CNTs binding proprieties in order to design a new platform for the detection of Palytoxin (PTX). Palythoa toxica, is known as one of the most potent marine toxins: human illness and fatalities have been reported after ingestion of PTX-contaminated tropical and subtropical fish and crabs . Recently, considerable traces of PTX have been regularly registered in some areas of the Mediterranean Sea, provoking in 2005 more than 200 cases of respiratory syndrome in patients exposed to marine aerosol on beach areas in Genoa, Italy.[3] Furthermore, these toxins have also been detected in seafood (mussels, clams and sea urchins) collected in the Mediterranean Sea.[4] Due to the high toxicological potential of PTX and its analogs we have focused the present research on the realization of an electrochemiluminescent sensor device for the PTX detection; wile our platform is extremely versatile and can be modified to detect many other biological analyte.

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COFFEE

Monday afternoon, 9 November, 15:30

Afternoon Session 2

Monday afternoon, 9 November, 15:55

Chair: Limoges, B. Vagin, M.Y.

15:55 Keynote lecture

Short and long range sensing on plasmonic interfaces

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Label-free detection schemes have become very popular for miniaturized sensing platforms as they offer a high possibility for the realization of more convenient bioassay systems, compared to conventional ones, which require labeling with enzymes, fluorescent dyes, etc. Surface plasmon resonance-based methods have shown their potential as label-free detection schemes as well as promising approaches for the fabrication of miniaturized optical sensors and devices.[1]

Conventionally, surface plasmon propagation on continuous thin metal films is exploited, where the surface selectivity arises from the enhancement of electrical fields at these metal surfaces through the formation of surface plasmon polaritons (SPPs). The other possibility for plasmonic sensing is based on the generation of non propagating localized surface plasmons on metal nanoparticles.[1] This technique known as localized surface plasmon resonance (LSPR) takes advantage of the fascinating optical properties of metal nanoparticles. The use of LSPR-based phenomena for chemical and biological sensing is of special interest, because it allows label-free detection of extremely small concentrations of target molecules.

Currently the focus is on the search of highly sensitive as well as optically and chemically stable LSPR interfaces. One of the commonly used techniques is nanoparticles coating with a dielectric layer. However, for dielectric-coated metallic particles, it is assumed that the LSPR shift exhibits essentially an exponential decay until saturation for dielectric layer thicknesses comparable to the particle size. This represents a major limitation for long range sensing.

In this presentation we will present different strategies for the formation of chemically and optically stable LSPR interfaces.[2-5] Our recent results on the possibility for short and long range for chemical and biological sensing will be discussed.[6,7] Finally, different strategies for linking of functional groups to the LSPR interfaces will be discussed.

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16:15 Keynote lecture

Bio-inspired Supramolecular Nano-Self Assemblies for Light Energy Conversion

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Recent research efforts are focused on the development of low-cost solar cells using organic/inorganic dye molecules in the presence/absence of additional electron donor/acceptor components. The basic working principle of organic solar cells based on electron donor-acceptor hybrids is the dissociation of photogenerated excitations at the interface between electron donor and acceptor phases by a photoinduced charge separation process with subsequent transport of the charge carriers in the respective phases to the electrodes. Critical parameters for the photocurrent generation include the wide-band absorption of the active layer, the efficiency of the charge transfer, and the transport of charge carriers in the materials involved. Several strategies have been developed to improve these parameters for efficient light energy harvesting.

Here, we wish to report self-assembly approaches to construct donor-acceptor hybrids for photovoltaic applications. In the first approach, photoelectrochemical behavior of fullerene, C_{60} self-assembled via axial coordination to an electrochemically polymerized zinc porphyrin film is systematically investigated to unravel the importance of the coordinated fullerene in improving the photocurrent and photovoltage generation of the resulting donor-acceptor dyad. In the second approach, ITO/TiO_2 surface is modified with imidazolyl benzoic acid to create an imidazole coordinating site. The imidazole is subsequently coordinated to various metallotetrapyrroles and dyads formed by these sensitizers. The importance of donor$_2$-donor$_1$ type dyad in improving the photovoltaic behavior has been successfully demonstrated.

16:35 Short communication

Increasing the surface area of electrodeposited-Pt through adding surfactant for dye-sensitized solar cell application

Yi-Hsuan Lai[1,2], Chia-Yu Lin[1], Chii-Wann Lin[2,3], Kuo-Chuan Ho[1,4]

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Counter electrodes, as one of important components in dye-sensitized solar cells (DSSCs), play a role of transferring electrons arriving from external circuit back to the iodide (I^-)/triiodide (I_3^-) redox electrolyte and to catalyze the reduction of the redox couple [1]. Although sputtered-platinum (SP-Pt) on conducting glass, such as ITO or FTO, was generally used as the counter electrode in DSSCs for I_3^- reduction, less attention has been paid to increase the active surface area for I_3^- reduction as well as the cell efficiency by controlling the morphology of Pt through adding the surfactant in the electrodeposition bath. .

In this study, a Pt counter electrode for ZnO-based DSSCs was prepared by electrochemical deposition of H_2PtCl_6 on ITO substrate in the presence of nonionic surfactant, *t*-octylphenoxypolyethoxyethanol (Triton® X-100). Triton® X-100 was selected to achieve an ordered structure for the electrochemically deposited Pt, which is based on the fact that a nonionic surfactant forms liquid crystalline phase that can be used as a template for the production of a well-defined mesoporous Pt [2]. Cyclic voltammetry (CV) was utilized here to compare the I^-/I_3^- redox behavior between the SP-Pt electrode and the electrodeposited-Pt (ED-Pt) electrode. Both the peak current density and the charge capacity for the ED-Pt film are larger than those of the SP-Pt film. This can be interpreted in terms of increased active surface area of this film. The ZnO-based cells fabricated with an ED-Pt counter electrode showed a higher conversion efficiency of 1.69% compared with cell fabricated with a SP-Pt (1.21%) counter electrode under the illumination of 100 mW/cm^2. The enhancement was attributed to the increase in the effective surface area of Pt for I_3^- reduction.

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16:50 Short communication

Photo-Electrochemical Investigation of Self-Organized TiO_2 Nanotubes

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In this presentation work investigating the photoelectrochemical behaviour of different types of self-organised layers of vertically oriented TiO_2 nanotubes will be presented and comparison to three-dimensional nanoparticle layers of similar thickness will be made. It will be shown that the conversion efficiency of bulk anatase TiO_2 can be improved by nanostructuring the electrode by a single electrochemical step followed by annealing. The role of the order and wall smoothness of the nanotubes produced by this electrochemical step on their photoelectrochemical behaviour will be discussed in the light of comparison between two different electrolytes used to produce nanotubes: i) aqueous electrolytes, where very rough nanotube walls are formed and ii) organic electrolytes, where nanotubes with much smoother walls are grown. The obtained results suggest a similar electron diffusion mechanism, under complete depletion conditions, for electrodes constructed from nanotubes or nanoparticles when illuminated with UV light. We propose a model pointing out the differences and analogies between nanoparticle and nanotube films in contact with an electrolyte, when illuminated with UV light. The lower number of grain boundaries through which the electrons have to pass in the case of nanotubes allows electron diffusion lengths of 24 µm, which are 30 times higher than for nanoparticles measured under the same conditions. However, the energetic states present in the band gap make the movement of the majority charge carriers, along the nanotube length, extremely slow: *i.e.* in the order of seconds. Such extended transportation times are not necessarily a loss mechanism. Indeed, the conversion efficiency of the nanotubes is not adversely affected by the length of the nanotubes for layer depths less than the electron diffusion length. These findings show the possibility of using nanotubes with a length of 20 µm in photoelectrochemical cells without having detrimental losses to efficiency due to electron-hole recombination. This is of high significance for photoelectrochemical applications of TiO_2 that rely on electron transport processes (such as dye sensitized solar cells, where the length of the nanotube layer defines the amount of the dye absorbed), providing a very high effective surface area and thickness, without significant losses.

17:05 Short communication

$MoSe_2$ Substrates for the Electrodeposition of CISe Semiconductor Films

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The semiconductor copper indium diselenide (CISe) has attracted considerable interest for use as an absorber in solar cells due to its high absorption coefficient (10^5 cm^{-1}) and useful band gap of 1.05 eV. On a laboratory scale, solar cells based on $CuInSe_2$ have reached efficiencies of 14.5% [1]. However, these use expensive and technically challenging techniques. One practical method for depositing thin films of copper indium diselenide is electro-deposition. Electrodeposition is viewed as a safe, clean and efficient deposition method and can be readily scaled up.

Typically, CISe films are electrodeposited onto Mo-coated substrates. The substrates serve as the back contact of the device. However, Mo is not chemically inert. Immersing the electrode in an acidic or alkaline plating solution (without applying a potential) will cause the Mo to dissolve or corrode. A new methodology to avoid this problem is to passivate the Mo film using a very thin layer of $MoSe_2$. Thin films of $MoSe_2$ are inert and highly conducting. Cyclic voltammograms for the $Ru(NH_3)_6^{3+/2+}$ and $In^{3+/0}$ redox systems at the $MoSe_2$ film coated electrodes were reversible.

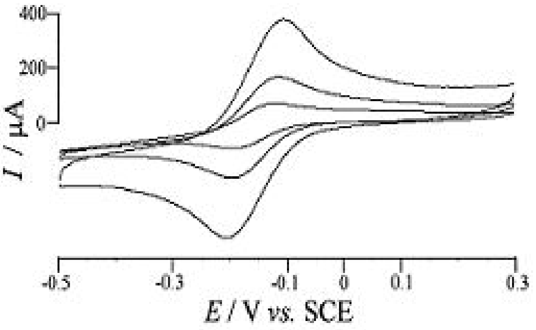

Figure 1: Reversible cyclic voltammograms of 1 mM $Ru(NH_3)_6^{3+}$ in 0.1 M KCl at a $MoSe_2$ electrode at potential scan rates 0.01, 0.05, and 0.2 V s^{-1}.

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17:20 Short communication

Silicon micro sensors as integrated readout platform for colorimetric and fluorescence based opto-chemical tranducers

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Opto-chemical transducer almost offers unlimited possibilities for detection of physical quantities. New technologies and research show a steady increasing of publications in the area of sensoric principles. For transfer to real world applications the optical response has to be converted into an electrical signal. An exceptional opto chemical transducer loses the attraction if complex and expensive instruments for analysis are requires. Therefore the readout system must be very compact and producible for low cost. In this presentation, the technology platform as a solution for these problems will be presented. We combine micro structuring of silicon, photodiode fabrication, chip in chip mounting and novel assembly technologies for creation of a flexible sensor platform. This flexible combination of technologies allow fabricating a family of planar optical remission sensors. With variation of design and modifications, we are able to detect colorimetric, fluorescent properties of an sensitive layer attached on the sensor surface. In our sensor with typical size of 6mm x 6mm x 1mm different emitting sources based on LED's or laser diodes, multiple detection cannels for the remitted light and also measurement of temperature are included. Based on this sensors we proof the concept by demonstrating sensors for oxygen, carbon dioxide and ammonia based on colorimetric and fluorescent changes in the transducer layer. In both configurations, LED's irradiated the sensitive polymer layer through a transparent substrate. The absorption or fluorescence properties of dyed polymer are changed by the chemical reaction and light response is detected by PIN diodes. The signal shift is analyzed by using a computer controlled evaluation board of own construction. Accuracy and reliability of the remission sensor system were verified and the whole sensor system was experimentally tested in the range of concentrations from 50 ppm up to 100 000 ppm for CO2 and O2 Furthermore, we develop concepts to use the sensor also for interferometric detection of layer properties and the combination with capacitive structures on the surface. This allows detecting of thickness or refractive index variation of layers in future.

17:35 Short communication

Silver Nanoparticle Catalysed NO_3^- Reduction Characterised with a Hydrodynamic Generator-Collector SPCE System

Richard Webster[1], Frank Marken[1], Matthew Jones[1], David J. Fermin[2], Robert J. Potter[3]

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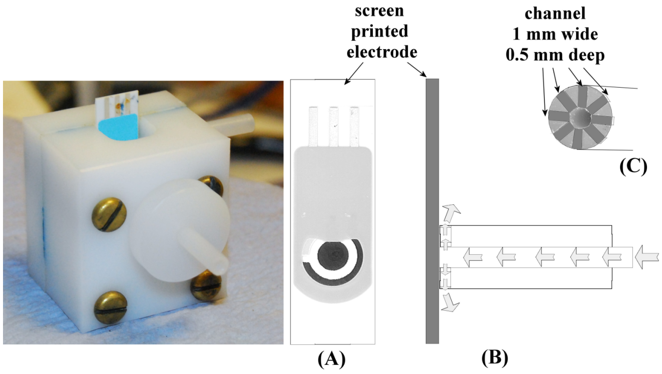
Silver nanoparticles are synthesised employing the tannin method and deposited onto the screen-printed carbon electrode (SPCE) with a solvent evaporation process. Cyclic voltammetry allows the amount (or total surface area) for nanoparticle assemblies to be determined. The silver nanoparticle aggregates are catalytically active for the reduction of nitrate to nitrite[1, 2] in aqueous 0.1 M NaOH. In order to investigate the efficiency and kinetics of the nanoparticle catalysed process, a hydrodynamic flow cell was designed and fabricated.



The flow cell allowed the reaction solution to be flowed across the SPCE and with the help of the $Fe(CN)_6^{4-/3-}$ redox system the diffusion layer thickness was calibrated. In the generator–collector mode, efficiency of the product formation was calibrated. For the nitrate reduction, close to 100% current efficiency was determined and the diffusion-controlled reduction was observed with a sufficiently high amount of the catalyst.

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17:50 Short communication

Chemiresistive-type NO gas sensor based on in-situ synthesized poly(3,4-ethylenedioxythiophene) film

Chung-Wen Lin[1], Chia-Yu Lin[2], Chi-An Dai[1,2], Kuo-Chuan Ho[1,2], Pei-Zen Chang[3]

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Nitric oxide (NO) is not only a toxic air pollutant generated in most combustion processes, resulting in the formation of ozone and acid rain, but also an important signaling molecule involved in many physiological and pathological processes within mammalian body of which the effect can be beneficial and/or detrimental [1]. Therefore, it is necessary to develop a reliable and sensitive sensor to fulfill the above mentioned environmental and biochemical concerns. In this study, 3,4-ethylenedioxythiophene (EDOT) and 3-thiophenecarboxylic acid (3-T acid) were in-situ oxidativelly copolymerized on a gold interdigitated electrode and the resulted films were used as a resistive type gas sensor. The effects of the composition, *ie.* the ratio of [3-T acid]/[EDOT], and the acid/base treatment on the sensor response were investigated. Our preliminary results showed that as the ratio of [3-T acid]/[EDOT] was increased from 0 to 3, the sensor response to the exposure of 50 ppm NO gas was increased from nearly none to a slightly higher value of 0.6 %. However, the sensor response can be dramatically increased from 0.6 % to 9.7 % if the in-situ synthesized film is to be treated with hydrochloric acid and ammonia sequentially during which the in-situ copolymer film is reduced. In addition, the selectivity of the NO gas sensor is significantly improved toward CO gas, in which there is essentially no response toward CO gas, which is in sharp contrast in observation with that of the NO gas sensor made from commercial Baytron® film. Further studies on the effects of acid/base treatment duration and film thickness on the sensor response to NO gas are in progress.

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DINNER

Monday evening, 9 November, 18:30

SOCIAL EVENT

Monday evening, 9 November, 19:30

Tuesday, 10 November

Morning Session 1

Tuesday morning, 10 November, 9:00
Chair: Ferapontova, E. Haga, M.

9:00 Tutorial lecture

Application of gold, silica and titania surfaces for the PM IRRAS: structural studies of biologically relevant films

Izabella Brand[1], Martina Nullmeier[1], Michael Ahlers[1], Sabine Szunerits[2], Rabah Boukherroub[3], Gunther Wittstock[1]

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Polarization modulation infrared reflection absorption spectroscopy (PM IRRAS) is an excellent tool for structural studies of organized organic layers on surfaces reflecting the IR radiation, such as Au or Pt. IR transmitting or absorbing substances such as silica, or titania are not suitable for IRRAS analysis. However, these surfaces are of large importance for implants development and design, creating a large need to understand properties of a biological substance on their surfaces. Despite the fact that silica and titania, depending on the wavelength of the IR light, are either transparent or absorptive to the IR radiation, when deposited in the form of thin films on a reflecting material such as gold fulfill surface selection rules.

The PM IRRAS is applied for structural analysis of bilayers of 1,2dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) deposited using the Langmuir-Blodgett and Langmuir-Schaefer techniques on gold, silica and titania surfaces. Lipid films formed on Au, Au|SiO$_2$ and Au|Ti|TiO$_2$ surfaces show two-dimensional long range order. The hydrocarbon chains exist in a liquid and a gel phase, depending on the surface pressure of the film transfer. Interactions between positively charged choline and the negatively charged silica and titania surfaces influence the arrangement of the polar head group of the lipid molecule at the interface. On the titania surface in a loosely packed bilayer the polar head group has an open conformation. In a densely packed bilayer on all surfaces interactions between the choline and phosphate groups of DMPC predominate interactions with the surface, changing the conformation of the polar head group.

A lipid bilayer exposed to the electric field mimics a natural cell membrane. The lipid bilayer assembled on the gold electrode was exposed to protein solutions interacting specifically either with a glycolipid or with a phospholipid. Charge accumulated on the membrane, capacity, potential window of film adsorption were determined electrochemically.

A successful adaptation of an implant material in an organism is governed by the adsorption processes of the extracellular matrix. The great success of titania implants is connected with a formation of collagen rich layer on its surface. The process of adsorption of collagen helices on the Au|Ti|TiO$_2$ surface was monitored by the PM IRRAS. In an electrolyte solution, however, a collagen coating is unstable. A significant improvement of the stability of the collagen layer was obtained, when the protein was coadsorbed with a polysaccharide (heparine) on the surface of titania pre-treated in 20 mM CaCl$_2$ solution. The PM IRRA spectra of collagen on the titania surface show a blue-shift of the amide I band, as compared to an IR spectrum in aqueous solution. The collagen helix is less hydrated / weaker hydrogen bonded in the adsorbed state, indicating that a hydrogen bonding network in the triple helix of collagen changes upon adsorption.

9:40 Keynote lecture

Attachment of gold nanoparticles on indium tin oxide for tuning nanostructured electrode interfaces

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The attachment of gold nanoparticles (AuNPs) on indium tin oxide (ITO) electrodes permits their electroanalytical applications because of the electrocatalytic ability and bio-compatibility of AuNPs. In recent years, we have been studying the fabrications of AuNP-attached ITO electrodes using a seed-mediated growth method, which was originally developed for the preparation of gold nanorods. In addition to the easiness of the wet chemical preparation at room temperature, with the seed-mediated growth method, it was a success that the charge transfer resistance can be reduced for thus fabricated AuNP-attached ITO electrodes, and also they are applicable to the attachment of hemeproteins. However, there is a difficulty in controlling the density of the attached AuNPs, though we tried several modified approaches in the seeding and the growth processes.

In the present work, for the purpose of the denser attachment of AuNPs on ITO electrodes, we tried to perform the nanostructuring of AuNPs on the ITO surfaces using linker molecules. In addition to the well-know linker molecules, 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminoptopropyltrimethoxysilane (APTMS), we used cysteamine because it is known that the linkage is possible via the bonding of S with the ITO surfaces. Systematic comparisons of the attached nanostructures of AuNPs on ITO were carried out after the room temperature treatment of the ITO surafaces in ethanoholic linker solutions followed by the room tenperature attachemnet of AuNPs using (i) one-step immersion into the 20-nm Au colloidal solution (Sigma) or (ii) two-step immersion, i.e., seed-mediated growth treatment.

Consequently, in the case (i), it was found that APTMS was suitable for the denser and homogeneous attachment of AuNPs on ITO surfaces keepin a dispersed state. In contrast, in the case (ii), the nanostructuring of AuNPs were possible with MPTMS and cysyeamine using the seed mediated growth, while the growth of AuNPs were quite smaller with the APTMS linker.

The differences of the attachment characteristics of AuNPs depending on the size were also observed. As the results, it was found that smaller AuNPs attached dominantly on the surface of ITO. The results of the competitive attachments of 5, 10, 20 nm AuNPs are presented.

10:00 Short communication

Electrochemical and SEIRA characterization of mercaptosuccinic acid monolayer on Au(111) further employed for cytochrome c immobilization

Agata Królikowska[1], Annia Kycia[2], Jie Li[2], Jay Leitch[2], Jolanta Bukowska[1], Jacek Lipkowski[2]

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The adsorption of mercaptosuccinic acid (MSA) on gold(111) surface in 0.1 M NaOH aqueous solution was examined with electrochemical methods and potential dependent in situ FTIR spectroscopy. Differential capacitance and chronocoulometry results indicated the multistep adsorption, proceeding with a slow rate. Gibbs isotherm was determined to evaluate the MSA Gibbs excess and to record the chronocoulometry curve for the MSA monolayer of known surface coverage, transferred by horizontal touch (HT) technique. The potential dependence of electrosorption valency (charge number per adsorbed molecule) was determined and it was found that its value is higher than unity for potentials above pzc. This result suggests that adsorption takes place not only through the gold-sulfur bond formation, but the interactions with the metal substrate via the carboxylate group is also very likely. The orientation of the MSA molecules on gold in contact with aqueous NaOH as a function of the potential was studied by RATIO method, using surface enhanced infrared reflection absorption (SEIRA) spectroscopy. An effort to extract the tilt angle separately for each of two MSA carboxylate groups was made. A schematic representation of MSA molecule adsorbed on Au, defining the determined tilt angle (γ) for one of the groups is shown in Figure 1. The model of MSA molecule adsorbed with one COO^- group (closer to the sulfur atom) directed towards the gold substrate and the second one exposed to the solution was proposed. MSA coated gold was successfully employed for electrostatic attachment of cytochrome c, preserving electroactivity of the protein, as verified with SEIRA spectro-electrochemical experiment. A deduced binding site of the cytochrome c by MSA molecules appears to be different than for monocarboxylate terminated alkanethiolates monolayers.

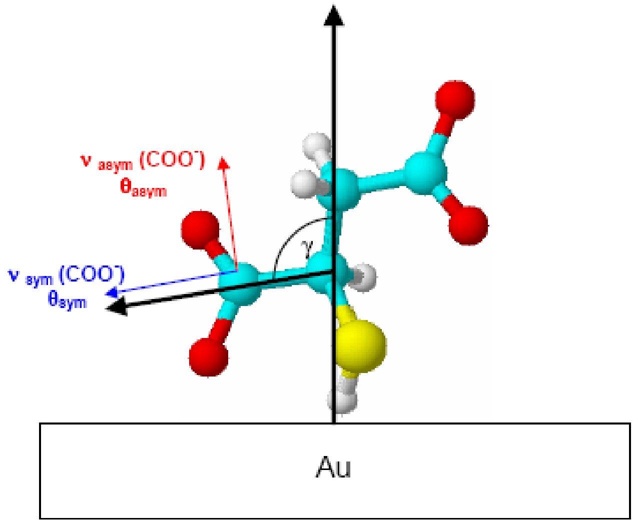

Figure 1

Schematic representation of mercaptosuccinate adsorbed on Au substrate (caution – the SH bond cleavage is not included) with the marked tilt angle γ and directions of the transition moments corresponding to the symmetric (blue arrow) and asymmetric (red arrow) carboxylate stretch.

10:15 Short communication

Electrochemical studies of the interaction of three component lipid bilayers with siglec protein

Martina Nullmeier[1], Hendrik Koliwer-Brandl[2], Soerge Kelm[2], Izabella Brand[1]

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A natural lipid membrane exists in a liquid state, but it forms a well ordered structure. The biological membrane contains solid, highly ordered aggregates, which are composed of cholesterol and glycolipids possessing large head groups composed of sugar and/or sialic acid residues.[1] Thereby glycosphingolipids, glycolipids containing at least one sialic acid residue, are proposed to be a binding partner for siglec proteins (sialic-acid binding immunoglobulin-like lectins), which are an important part of the immune system. In this study Siglec-4, the myelin-associated glycoprotein (MAG) is relevant.[2]

Unsymmetric three component lipid bilayers containing 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC), 30 mol % of cholesterol and 20 mol % of GD1a ganglioside were prepared on the gold surface. To produce the mixed lipid bilayer vertical Langmuir-Blodgett and horizontal touch Langmuir-Schaeffer methods were used. The produced lipid layer contains the ganglioside only in the outer layer, mimicking a natural cell membrane. Under physiological conditions the lipid membrane is constantly exposed to high electric fields. The stability, potential window of the adsorption of the three component lipid bilayer and the phase transition in the film were tested in the electrochemical cell. Next, the lipid bilayer was exposed to the electrolyte solution containing up to 2 μg/ml MAG siglec protein. The interaction was studied measuring the differential capacitance over a period of several hours. Without the protein present in the solution the capacitance increased over time and the phase transition is found at -0.38 V vs. Ag/AgCl reference electrode. This result indicated that a three component lipid bilayer is not very stable when exposed to electric field. A lowering of the capacitance was observed, indicating that the binding of the protein stabilizes the lipid bilayer. Moreover, upon interaction with the siglec protein the potential of the phase transition is shifted to -0.64 V vs. Ag/AgCl. This result also shows a stabilization of the lipid membrane and its higher resistance to the electric field.

The polarization modulation infrared reflection absorption spectroscopy (PM IRRAS) was used to confirm binding of the protein to the lipid bilayer. The IRRA spectra were collected from lipid bilayers in which the outer-layer was exposed to the solution containing the MAG protein. The amide I and amide II bands are clearly seen in the spectra, indicating attachment of the siglec protein to the lipid bilayer.

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COFFEE

Tuesday morning, 10 November, 10:30

Morning Session 2

Tuesday morning, 10 November, 10:55

Chair: Touahir, L. Actis, P.

10:55 Short communication

Study of the interfacial properties of calixarenes and their interaction with dopamine in mixed phospholipid monolayers

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Calix[n]arenes are macrocylic compounds derivated from the synthesis of phenols and aldehydes, where [n] refers to the number of the macrocyclic cycles. The characteristic feature of calix[n]arenes is the presence of the hydrophobic cavity lending them ability to recognize metal ions, organic molecules, proteins and other ligands[1-3]. Herein we present the results of the study of the physical properties of monolayers formed by calix[4]resorcinarenes and their mixtures with dipalmitoyl phosphatidylcholine (DPPC) formed at the air/water interface. We also studied the mechanisms of interaction of calixarenes with neurotransmitter dopamine. For this purpose we applied the methods of measurement surface-pressure area isotherms, surface potential and Maxwell displacement currents (MDC).[4,5] Due to their amphiphilic nature both calix[4]arene and DPPC form stable monolayers. For mixed monolayers, increase of the content of calixarenes in the monolayers resulted in increase of the mean molecular area and decrease of the compressibility modulus. We also observed immiscibility of both components in the mixed monolayers at all the molar ratios studies, mainly at the higher surface pressure when the monolayers were in the solid state. Presence of dopamine in the subphase resulted in the increase of the mean molecular area and in decrease of the monolayer compressibility modulus, which suggest destabilization of the calixarene monolayers. This could be due to the binding of the dopamine inside the hydrophobic cavities of calix[4]resorcinarenes, weakening thus the strength of the lateral forces acting between the adjacent molecules in the monolayer. Moreover, MDC was used for the first time to study changes in the charge state of the monolayers. Dipole moment of calix[4]resorcinarene in the presence of dopamine, as analyzed by MDC, reached the maximum value in the phase transition from liquid to solid phase, which suggests the binding of dopamine depends on the surface pressure, and hence on the orientation of the calix[4]arene in the monolayer. However, quantification of the excess of Gibbs free energy of the mutual calix[4]resorcinarene-dopamine bond implies weak interactions.

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11:10 Short communication

Impedimetric RNA assay – detection of the activity of a hairpin ribozyme

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The hairpin ribozyme belongs to a group of small catalytic RNA structures which is derived from the (-)-strand of the Tobacco ring spot virus satellite RNA. Here, we propose an electrochemical detection system for monitoring of the ribozyme activity using electroche¬mical impedance spectroscopy (EIS). For this purpose, a thiolated RNA substrate is self-assembled at a gold surface. Incubation with the hairpin ribozyme leads to the formation of Watson-Crick base pairs between the ribozyme and its complementary substrate and thus to an assembly of the ribozyme at the RNA substrate monolayer. Cleavage of the substrate which is leading to a disintegration of the ribozyme/substrate complex can be initiated by addition of Mg^{2+} ions.

The cleavage reaction is monitored by EIS by studying the modulation of the charge transfer resistance of a free-diffusing redox mediator ($[Fe(CN)_6]^{3-/4-}$). The access of the free-diffusing and negatively charged redox mediator is modulated due to the chemisorption of the thiolated RNA and the subsequent formation of the RNA/ribozyme complex, which manifests as an increase in the charge transfer resistance in the impedance signal. Upon addition of Mg^{2+} ions the charge transfer resistance decreases again due to the cleavage reaction.

This strategy can be applied for the selection of a specific ribozyme sequence from a RNA library. This concept is evaluated by immobilizing the RNA substrate at a macroscopic gold electrode surface, assembling of the complementary hairpin ribozyme structure at the monolayer and initiating the cleavage reaction by addition of Mg^{2+} ions. The products of the cleavage reaction, namely the ribozyme and the cleaved part of the RNA substrate, are collected. The RNA is then reverse transcribed into cDNA, amplified by means of PCR and analyzed by sequencing. First results are showing that the ribozyme which was previously assembled at the RNA substrate modified surface was found in the collected solution.

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11:25 Short communication

Surface manipulation and immobilization of single DNA wire on Au surface

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DNA alignment techniques have been required in order to analyze its genetic code and to use DNA as a one-dimensional wire template. Although several methods of DNA alignment had been reported previously, for example electrophoresis, transfer-printing on polydimethylsiloxane, and molecular combing, it was difficult to control the number and position of DNA on a solid surface. In this study, we introduce a new methodology for DNA alignment using Nd: YAG laser (1064 nm). We observed for the first time that focusing of Nd: YAG laser beam on Au thin film surface induced a rapid pulling of DNA molecules near the focal point in handmade liquid cell. l DNA was stained with SYBR Gold for fluorescence microscope observation. One end of l DNA strands was labeled with thiol and immobilized by self-assembly of thiol group on an Au surface. After the immobilization, the other end of strands was free in solution, and the elongation was observed near the laser focal point as shown in Fig 1. In the case of bare Au surface, the elongated DNA was pinned upon a touch of laser focal point with the elongated edge of DNAs. On the other hand, on the bovine serum albumin modified Au surface DNA was not pinned. The present laser pulling phenomenon was strongly dependent on the thickness of Au film and the solid substrate. This optical manipulation method opens the door to fabricating single DNA nanowires and junctions.

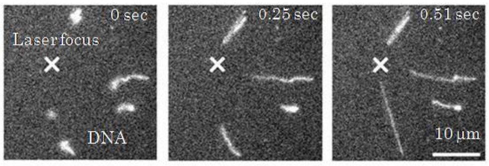

Fig. 1 Temporal change on fluorescence microscope image of one-end immobilized dsDNAs in liquid cell

11:40 Short communication

Enzyme-amplified amperometric DNA hybridization assay based on bioelectrocatalysis using redox-polymer modified electrodes

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Electrochemical detection of DNA hybridization is viable alternative to optical and radio-labelled techniques. The benefits of using biosensors based on electrochemical systems are high sensitivity, possible development of miniature systems interfaced to electronic devices as well as low cost of operation and small sample requirements.

We have developed an electrochemical DNA hybridization assay, based on deposition of films, consisting of single-strand DNA cross-linked with an osmium-based redox polymer, on gold electrodes. A signal, corresponding to hybridization between the immobilized probe ssDNA and a biotin-conjugated target DNA is amplified by addition of glucose oxidase-avidin conjugate and glucose substrate[1]. The interaction between target DNA, avidin-GOx and osmium redox polymer layer generates a bioelectrocatalytic current in the presence of glucose. Catalytic currents corresponding to oxidation of glucose scale with complementary DNA concentration.

An improvement in recognition layer stability is achieved by providing an anchoring layer of cysteamine, via self-assembly, onto the underlying gold electrode. Further improvements in layer stability may be achieved by modification of carbon electrodes via aryl diazonium electroreduction to provide a grafted anchoring layer [2].

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11:55 Tutorial lecture

Strategies for Self-Assembly of Phospholipids at Interfaces

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Phospholipids are the primary constituent in lipids bilayer structures, and are used in the construction of biomimetic interfaces. The physical deposition of lipid bilayers on planar substrates results in structures that are not physically robust, and there have been a variety of methods used to bind lipids to interfaces. In this talk I will describe some of the recent efforts of my research group in forming self-assembled lipid bilayer structures, where the lipids are bound chemically to the interface. This strategy can be used on either metallic or dielectric interfaces, depending on the binding chemistry used.

One method of lipid binding we will discuss are covalent bonding of lipids to metallic substrates using thiol/gold chemistry, and the limits imposed on this approach by the morphology of liposomes used in the deposition process. Another method is the use of metal-phosphate complexation chemistry on surfaces that have been modified to produce a phosphate-terminated interface. These methods result in interfaces with different physical properties, which we will discuss.

LUNCH

Tuesday afternoon, 10 November, 13:00

Departure

Tuesday afternoon, 10 November, 14:00

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