

SCIENTIFIC REPORT

Conference: Electrochemistry and Self-Assembly for Nanomaterials Science, organised in honour of Prof. **Israël RUBINSTEIN** (Weizmann Institute of Science, Rehovot, Israël)

Date and Location: 29-30/08/2007, University of Namur, Belgium.

Conference Chairs: Profs. Zineb MEKHALIF (FUNDP) and Christian AMATORE (ENS)

Local organizers: Prof. J. DELHALLE and the PhD and Post-Docs members of the CES laboratory (Christelle ARNOULD, François BERGER, Balazs CSOKA, Jessica DENAYER, Vincent DE NOOSE, Simon DETRICHE, Sebastien DEVILLERS, Gregory FONDER, Antonio FONSECA, Charlotte GUISSSET, Tatiana ISSAKOVA, Isabelle MINET, Jean-François SEFFER Jorge MEJIA MENDOZA), Daniel LEMAIRE (Chemistry Department) and Z. MEKHALIF.

Co-sponsored by:

FUNDP (University of Namur)

International Society of Electrochemistry (ISE, divisions 1 and 7)

FNRS (Fonds National de la Recherche Scientifique)

ALCHIMER

CARDIATIS

IJ CAMBRIA

BENELUX SCIENTIFIC

AMATEK

BRUKER

WILEY

A special issue of invited papers will appear in the Journal of Electroanalytical Chemistry and is dedicated to Israël RUBINSTEIN for his 60th birthday.



Israël Rubinstein



Zineb Mekhalif, Israël Rubinstein, Christian Amatore

Scientific PROGRAM

Opening Honorary Lecture

From Electrochemistry to Nanochemistry: my First 38 Years of Research

Israël RUBINSTEIN

Weizmann Institute of Science, Rehovot, Israel

12 Plenary Lectures

Seeing Electronic Communication within Molecules

Christian AMATORE

Ecole Normale Supérieure, Paris, France

Electrochemistry of Single Molecules - Single Molecule Spectroelectrochemistry and other Approaches

Allen J. BARD

University of Texas, Austin, USA

From Model to Complex Self-Assembled Monolayers for Supramolecular Chemistry at Electrodes

Claudine BUESS-HERMAN

Université Libre de Bruxelles, Brussels, Belgium

Nanoparticle Assembly and Reactivity at Polarised Liquid|Liquid Interface

Hubert GIRAULT

Ecole Polytechnique Fédérale de Lausanne, Switzerland

Nanomaterials at Interfaces: an 18 Year-Long Journey

Yuval GOLAN

Ben-Gurion University, Beer Sheva, Israel

Conducting Polymer/Metal Nanocomposites

Jiri JANATA

Georgia Institute of Technology, Atlanta, USA

Molecular Printboards

David REINHOUDT

University of Twente, Enschede, Netherlands

Self-Organized TiO₂-Nanotube Layers: Formation, Properties, Applications

Patrik SCHMUKI

University of Erlangen-Nuremberg, Germany

In situ Visible-Infrared Sum Frequency Generation, a Probe of the Electronic and Vibrational Properties of the Electrochemical Interface

Abederrahmene TADJEDDINE

Université Paris-Sud Orsay, France

Applications of Localized Surface Plasmon Resonance Spectroscopy

Alexander VASKEVICH

Weizmann Institute of Science, Rehovot, Israel

Self- and Directed Assembly of Functional Nanoscale Structures

Paul S. WEISS

Pennsylvania State University, USA

Molecular Self-Assembly, from Active Metals to Carbon Nanotubes Surfaces

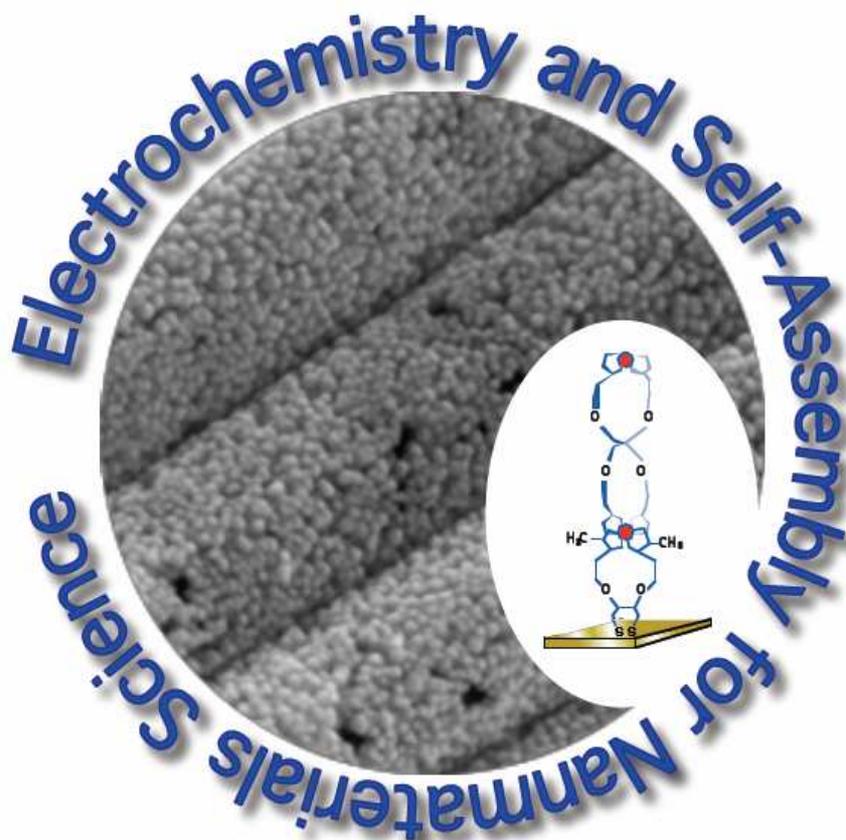
Zineb MEKHALIF

Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium

48 Poster presentations: Abstracts are reported in the full booklet below.



ESA - Nanomaterials 2007



Conference Chairs
Zineb MEKHALIF and Christian AMATORE

August 2007, 29-30
FUNDP, Namur, Belgium

<http://www.fundp.ac.be/esa-nanomaterials>

Schedule

2007 August 29th

8h00	Registration	
8h30-9h	Welcome Philippe Lambin Dean of the Science Faculty	
	Speaker	Chairman
9h-9h50	<i>Israel Rubinstein</i>	<i>Joseph Delhalle</i>
9h50-10h30	<i>Allen J. Bard</i>	<i>Christian Amatore</i>
10h30-11h	Coffee break	
11h-11h40	<i>Christian Amatore</i>	<i>Wolfgang Schuhmann</i>
11h40-12h30	<i>David Reindhout</i>	
12h30-14h30	Lunch	
14h30-15h10	<i>Alexander Vaskevich</i>	<i>Philippe Hapiot</i>
15h10-15h50	<i>Abderrahmene Tadjeddine</i>	
15h50-18h00	Poster Session, French Wine, Belgian Beers and Cheese	
19h30	Banquet	

2007 August 30th

	Speaker	Chairman
9h10-9h50	<i>Charles Martin</i>	<i>Gunther Wittstock</i>
9h50-10h30	<i>Hubert Girault</i>	
10h30-11h	Coffee break	
11h-11h40	<i>Claudine Buess-Herman</i>	<i>Luisa Abrantes</i>
11h40-12h20	<i>Yuval Golan</i>	
12h20-14h20	Lunch	
14h20-15h	<i>Paul S. Weiss</i>	<i>Cynthia Zoski</i>
15h00-15h40	<i>Jiri Janata</i>	
15h40-16h20	Coffee break	
16h20-17h00	<i>Patrik Schmuki</i>	<i>Davide Bonifazi</i>
17h00-17h40	<i>Zineb Mekhalif</i>	
17h40	Closure drink	

Sponsors



PLenary Lectures

Opening Honorary Lecture

From Electrochemistry to Nanochemistry: my First 38 Years of Research

Israël Rubinstein

Weizmann Institute of Science, Rehovot, Israel

The conference is organised by the Ecole Normale Supérieure de Paris (ENS) in collaboration with the Laboratoire de Chimie et d'Electrochimie des Surfaces (University of Namur, FUNDP) in honour of Professor *Israël RUBINSTEIN* on the occasion of his 60th birthday. This event is a special opportunity to acknowledge Israël RUBINSTEIN's scientific achievements in the fields of electrochemistry and self-assembly which he pioneered.

Electrochemistry of single molecules - Single molecule spectroelectrochemistry and other approaches

Allen J. Bard, Xiaoyin Xiao, Fu-Ren Fan, Rodrigo Palacios, and Paul F. Barbara

Department of Chemistry and Biochemistry, Center for Electrochemistry and Center for Nano- and Molecular Science and Technology
The University of Texas at Austin
Austin, Texas 78712

Much recent research has involved studies of single molecules or nanoparticles (NPs), because these can provide information that is not readily available from the more usual investigations of large ensembles. While most of these studies have dealt with the spectroscopic properties of molecules, we have been interested in the possibility of single molecule and particle electrochemical studies and will describe an overview of this research and recent results.

One new approach to the determination of the thermodynamics and kinetics of electron transfer (et) to single immobilized polymer molecules is based on single molecule spectroelectrochemistry (SMS-EC). SMS-EC measures electrochemical behavior one molecule at a time, offering for the first time the distribution of key electrochemical variables, e.g. the half-wave potential, $E_{1/2}$, not just the ensemble average. The experiments employ an electrochemical cell with a transparent (ITO) working electrode on which is immobilized, e.g. in a polymer film, the molecules of interest, a gold counter electrode, and a silver wire quasireference electrode (QRE) within a SMS apparatus. The fluorescence of the immobilized single molecules is monitored as a function of the working electrode potential, where et events cause a decrease in the emission of the molecule.

Experiments of single molecules and NP aggregates of the organic conjugated polymer poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and other molecules used in solid state electrochemical cells (OLEDs) will be described. The application of the technique to observation of single et events of ground state molecules and to studies of et to excited states will be discussed.

A different direct electrochemical approach involves observing collisions of metal NPs with the electrode by using a novel current amplification scheme. This has the potential to study single particle events and probe details of the nature of the charge transfer process at the electrode surface.

Electrochemistry within molecules: seeing intramolecular electronic communication

Christian Amatore

Ecole Normale Supérieure. Département de Chimie. UMR CNRS 8640
24 rue Lhomond. F-75231 Paris Cedex 05. France
<http://www.chimie.ens.fr/w3amatore/>
e-mail: christian.amatore@ens.fr; Ph: int+33-1-4432-3388; Fax: int+33-1-4432-3863

The concept of electronic communication (as opposed to electronic delocalization) is discussed and established on the basis of direct and in-time monitoring of electron hopping within molecules. This concept is then shown to be useful for the design of a new class of bio-organometallic drugs.

The basic principles allowing undistorted cyclic voltammetry up to $2.5 \text{ MV}\cdot\text{s}^{-1}$ to be performed at ultramicroelectrodes are recalled. Access to this range of ultrahigh scan rates allows nanosecond-time scale to be explored voltammetrically which offers obvious kinetic advantages by widening the mechanistic scope of voltammetry so that it encompasses now more than nine orders of magnitude.

In this paper, we are interested in discussing a remarkable—but less promoted—advantage of ultrafast voltammetry. Indeed, scan rates in the megavolts-*per*-second range allow the creation of diffusion layers with a maximal extension of a few nanometers, *viz.*, which are comparable to the size of chemical and biological molecules. In other words, this allows the *in-situ* and *direct* monitoring of redox communication *within* molecules.

The experimental validity and the interest of this concept are presented on the basis of two typical examples. One deals with the rate of redox commutation within self-assembled monolayers of diluted organic and organometallic molecules bearing a redox terminal group. This will exemplify that under some circumstances the electron transfer is controlled by the movement of an ion which is required to counterbalance the charge. This movement may be slowed down when the redox center is immersed within the diluent lipophilic chains.

The second application concerns the monitoring of the time-progression of electron-hopping diffusion through electron exchange between $64 \text{ Ru}^{\text{II/III}}(\text{tpy})_2$ redox groups distributed on a fourth generation PAMAM dendrimer molecule adsorbed onto an ultramicroelectrode. Besides the measurement of the rate of communication between adjacent ruthenium centers within one dendrimer, the method is extremely informative about the topology of the spatial arrangement of the 64 redox centers, so that it can be used as a molecular microtome with a resolution better than that of STM. Taking advantage of this system we investigate theoretically the frontier between stochastic and statistical behavior. Indeed, the size of these dendrimers (ca. 10 nm) is close from the smallest sizes of nanoelectrodes which can be built reliably today. Therefore, today one may ask the following question: How many molecules do we need to observe an average molecular behavior?

Molecular printboards

David N. Reinhoudt

Laboratory of Supramolecular Chemistry and Technology
MESA⁺ Research Institute for Nanotechnology
University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

Nanotechnology is a part of the chemical domain, because the ultimate goal is to build nanostructures with precision at the molecular level. This requires the ability to manipulate and modify molecules individually level rather than in the bulk. There are many challenges for chemists and in particular for supramolecular chemistry. In our group we are studying several aspects that may contribute to the bottom-up approach to nanostructures. Firstly, molecular printboards will be discussed that can be used to confine molecules in time and space. These printboards are self-assembled monolayers of receptor molecules on flat surfaces. The regular molecular assemblies offer anchoring points for (individual) molecules that can be immobilized (and erased) by supramolecular host-guest interactions. Suitable printboards are composed of cyclodextrine derivatives, immobilized on gold or glass surfaces. By force-distance spectroscopy we can analyse the forces involved between individual guest molecules and these receptors. Subsequently we can write or print guest molecules like dendrimers on these printboards by softlithographic techniques (microcontact printing and dip pen or nano-imprint lithography). We can also use layer-by-layer assembly processes and metal deposition in order to extend 2D-patterns to 3D-objects. By using these assembly processes we are able to fabricate electronic devices.

Finally, covalent chemistry has been recently developed for similar purposes. Both imine and click chemistry on SAMs will be discussed.

- 1) *J. Am. Chem. Soc.*, 2005, 127, 7594-7600
- 2) *J. Am. Chem. Soc.*, 2004, 126, 17050-17058
- 3) *J. Am. Chem. Soc.*, 2004, 126, 12266-12267
- 4) *Angew. Chem. Int. Ed.*, 2006, 45, 5292-5296

Applications of localized surface plasmon resonance (LSPR) spectroscopy

Alexander Vaskevich

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel
alexander.vaskevich@weizmann.ac.il

Nanostructured gold and silver films show a localized surface plasmon (SP) resonance, resulting in enhanced light scattering, the appearance of a SP absorption band, and enhancement of local electromagnetic fields. These unique properties have been used in various applications, including chemical and biological sensing as well as enhanced surface spectroscopies.

One of the problems in the development of practical devices based on localized surface plasmon resonance (LSPR) spectroscopy is preparation of stable and sensitive transducers using a simple and reproducible technology.¹ Our group has developed transmission LSPR (T-LSPR) transducers prepared by evaporation of discontinuous metal films onto transparent substrates.^{2,3} We have carried out a detailed study of Au and Ag island films, characterized using AFM, high-resolution SEM and cross-sectional TEM. Structural reshaping of metal island films, enabling tuning and optimization of their optical properties, was attained by thermal, chemical and electrochemical treatments.

The refractive index sensitivity and distance dependence of the T-LSPR response of Au island films were studied using different liquid media and a coordination-based self-assembled multilayer of a variable thickness, respectively. The sensitivity of an optimized Au island film remained nearly constant at distances of >15 nm from the Au island surface, providing flexibility in the design of T-LSPR based sensing interfaces.⁴ Tuning of the island size and shape allowed us to reach the highest LSPR refractive index sensitivity reported to date, i.e., 500 nm/refractive index unit (RIU). Encapsulation of Au island films in a 1.5 nm silica shell stabilizes the islands, such that the optical response is sensitive only to changes in the effective refractive index of the immediate environment.⁵

T-LSPR transducers based on evaporated metal island films present a general platform for research and practical applications. Its use in studies of the kinetics of surface processes as well as in gas sensing, DNA hybridization and specific protein recognition, will be demonstrated.

1. A. Vaskevich and I. Rubinstein, *Localized Surface Plasmon Resonance (LSPR) Spectroscopy in Biosensing*, in *Handbook of Biosensors and Biochips*, R. Marks, D. Cullen, C. Lowe, H. H. Weetall, I. Karube (Eds.), Wiley-VCH, in press.
2. G. Kalyuzhny, M. A. Schneeweiss, A. Shanzer, A. Vaskevich and I. Rubinstein, *J. Am. Chem. Soc.* **123** (2001) 3177.
3. G. Kalyuzhny, A. Vaskevich, M. A. Schneeweiss and I. Rubinstein, *Chem. Eur. J.* **8** (2002) 3850.
4. I. Doron-Mor, H. Cohen, Z. Barkay, A. Shanzer, A. Vaskevich and I. Rubinstein, *Chem. Eur. J.* **11** (2005) 5555.
5. I. Ruach-Nir, T. A. Bendikov, I. Doron-Mor, Z. Barkay, A. Vaskevich and I. Rubinstein, *J. Am. Chem. Soc.* **129** (2007) 84.

Sum Frequency Generation as a vibrational probe of the interface and thin films

A.Tadjeddine¹, B. Busson² and C. Humbert²

¹UDIL-CNRS, Centre Universitaire Paris-Sud, Bât. 201/P1, B.P.34, 91898 Orsay cedex, France
abderrahmane.tadjeddine@udil.u-psud.fr

²LCP/CLIO, CNRS-Université Paris-Sud, Orsay (France)

Understanding the nature and structure of surfaces and interfaces at a molecular level is of primary interest in a wide range of domains such as polymer adhesion, membrane biochemistry, catalysis...

Among the surface analysis tools available, infrared-visible sum-frequency generation (SFG) vibrational spectroscopy is of unique interest especially in the case of buried interfaces. SFG spectroscopy is based on the fact that second order non-linear optical processes are forbidden in the bulk of centrosymmetric media. At the interface between such media the centrosymmetry is broken and second order processes such as SFG are allowed. Therefore this technique is inherently surface (or interface) specific. Moreover the signal is enhanced when the frequency of the photons of one of the two pump laser beams matches the frequency of an allowed transition (vibrational or electronic) at the interface. Using a tunable infrared laser beam as one of the two pump beams, one can have access to the vibrational properties of the interface and to identify adsorbed species or to gain insight into the interfacial structure or charge transfer. Using short laser pulses and pump-probe schemes allows to study vibrational relaxation at interfaces and to explore the couplings between vibrational and electronic degrees of freedom in the case of adsorbates on a metallic substrate for example. Finally, recording the SFG response at different visible wavelengths yields unique information on the electronic and the vibrational properties of the interface..

After a brief description of the new developed set-up we have developed at the CLIO-Free Electron Facility (Orsay), we shall present and discuss some selected results recently obtained on the following topics:

- dissociative adsorption of methanol and ethanol at the platinum single crystal electrode-acidic solution: attention will be focused on the effects of the electrode surface orientation and the alcohol concentration on the structure of the interface and its evolution with the applied potential.
- the study of copper electrodes in contact with aqueous solutions containing 4-{2-[1-(2-cyanoethyl)-1,2,3,4-tetrahydroquinolin-6-yl]diazenyl} benzonitrile (CTDB) combining 2C-SFG, SERS and DFT calculations.
- the evolution of electronic and vibrational properties the Thiophenol/Ag(111) interface from the single monolayer to a thin multilayer, and the different vibronic coupling of the vibration modes in the 1000 cm⁻¹ spectral range.
- the behaviour of thin films of twelve molecular layers of chiral helicenebisquinone molecules in the energy range of phenyl ring vibrations (around 1600cm⁻¹) which show a measurable absorption in the visible range related to their supramolecular organization.

Nanoscience in bioanalytical chemistry - nanopore and nanotube resistive-pulse sensors

Charles R. Martin

Department of Chemistry
Center for Research at the Bio/Nano Interface
University of Florida
Gainesville, FL 32611

There is increasing interest in the concept of using nanopores as the sensing elements in resistive-pulse-based biosensors. The nanopore most often used is the α -hemolysin protein channel, and the sensor consists of a single channel embedded within a lipid bilayer membrane. An ionic current is passed through the channel, and analyte species are detected as transient blocks in this current associated with translocation of the analyte through the channel – resistive-pulse or stochastic sensing. While this is a promising sensing paradigm, it would be advantageous to eliminate the very fragile lipid bilayer membrane, and perhaps to replace the biological nanopore with an abiotic equivalent. We will describe biosensors based on conically shaped synthetic nanopores and nanotubes prepared by the track-etch method.

In one approach, gold nanotubes are deposited within the nanopore, which allows for easy biofunctionalization of the nanotube surfaces with small molecules, proteins, DNA, and other biomolecules. Such surface-bound biomolecules can act as molecular-recognition agents for binding analyte molecules to the tube walls, and this has allowed us to develop a new paradigm for protein biosensing. Three different molecular-recognition agents, and correspondingly three different protein analytes, have been investigated (i) biotin/streptavidin, (ii) protein-G/immunoglobulin, and (iii) an antibody to the protein ricin with ricin as the analyte. In all three cases, the molecular-recognition agent binds the analyte essentially irreversibly, and the analyte is detected as a permanent blockage of the ion current flowing through the nanotube. Alternatively analyte species can be driven electrophoretically through the unmodified conical nanopore and detected via the conventional resistive-pulse sensing paradigm. We have detected small molecules, DNA and proteins this way. Finally, the middle ground can be exploited; i.e., the nanotube can be functionalized with a selective but relatively weak-bind molecular-recognition agent. This leads to resistive-pulse sensing data where the current-pulse magnitude is related to the kinetics of release of the analyte from the molecular-recognition agent. We will discuss an example where the molecular-recognition agent is folate-binding protein and the analyte is folic acid.

Nanoparticle assembly and reactivity at polarised liquid|liquid interfaces

Mohamad Hojeij, Bin Su and Hubert H. Girault

Laboratoire d'Electrochimie Physique et Analytique, Station 6,
Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne
*Hubert.Girault @epfl.ch

Since the early work of Nernst more than a century ago, electrochemistry at the Interface between Two Electrolyte Solutions (ITIES) has developed into a rather mature area of research with many groups active in the field. From a structural viewpoint, a liquid|liquid interface is by definition a dynamic one, and hence a highly reproducible interface to study. Electrocapillary and capacitance measurements can be used to characterise the potential distribution in the absence or in the presence of specific adsorption.

Here, we shall present the functionalisation of polarised liquid/liquid interfaces by nano-objects such as metallic, semiconductor or organic nanoparticles. We shall for example show how the adsorption of these nano-objects can be potentiostatically controlled. The main reactivity we shall address is oxygen reduction and photo-energy conversion using either porphyrin assemblies or quantum dots as sensitizers. In particular, we shall present oxygen reduction data obtained in the presence of cobalt tetraphenylporphyrin, and photocurrents data obtained with CdSe nanoparticles.

Also, we shall show that it is possible to form thin liquid films on a solid support so as to obtain liquid|liquid interfaces supported on a solid electrode. Different strategies can be used including the layer-by-layer deposition of thin aqueous polyelectrolyte layers, or the sol-gel deposition of aqueous gels. When using a porous solid support, we can obtain pseudo-3D liquid-liquid interfaces.

From Model to Complex Self-Assembled Monolayer for Supramolecular Chemistry at Electrodes

Claudine Buess-Herman, Thomas Doneux*, Marc Steichen,

Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles, Faculté des Sciences, Boulevard du Triomphe, 2 CP 255, B-1050 Bruxelles, BELGIUM
E-mail: cbuess@ulb.ac.be

The formation of Self-Assembled Monolayers (SAMs) has become a very popular method to modify metallic surfaces. For many applications, monolayers have to be composed of the surfactant of interest mixed with a spacer in order to confer specific properties to the electrode. The variation and control of the relative quantities of different surfactants enabling the preparation of complex structures are therefore presently a subject of growing interest.

In our group we have considered first a model system composed of mixed self-assembled monolayers containing 2-mercaptobenzimidazole (MBI) and a negatively charged derivate 2-mercaptobenzimidazole-5-sulfonate (MBIS). The behaviour towards electron transfer of self-assembled monolayers of MBI or MBIS was first examined by cyclic voltammetry. The influence of the monolayers was drastically dependent on the charge of the redox probe used. On the MBI modified electrode, no inhibition is observed for $[\text{Fe}(\text{CN})_6]^{3-}$ probe, while it is markedly inhibited on the MBIS modified surface. When $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is used, a post-adsorption peak characteristic of the adsorption of the redox probe is detected only in at the MBIS modified electrode. Taking advantage of this difference, AC voltammetry has been used to determine the surface composition when mixed monolayers are formed by immersion of the gold substrate in mixtures of different molar fractions of MBI and MBIS.

Cationic $[\text{Ru}(\text{NH}_3)_6]^{3+}$ complexes are also known to bind electrostatically to the anionic DNA backbone. As a result, chronocoulometry can also be used to determine the amount of linear and hairpin DNA immobilized on polycrystalline gold electrodes in mixed SAMs of thiolated single-stranded oligonucleotides (HS-ssDNA) and a spacer (4-mercaptobutan-1-ol).

To obtain a clearly detectable label free hybridization signal, cysteine-SH modified PNA probes were immobilized in a mixed monolayer self-assembled together with 4-mercaptobutan-1-ol on the gold electrode. Peptide nucleic acids (PNA) are structural DNA analogues containing a neutral N-(2-aminoethyl)-glycine pseudopeptide backbone and show higher specificity in DNA recognition. Results show that the binding isotherm of the cationic metal complex to the surface-confined PNA-DNA duplex fits the Langmuir adsorption model. As a result, the binding constants of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ to immobilized PNA-DNA are derived from the experimental isotherm. The electron transfer kinetics of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ complex on the PNA modified electrode after DNA hybridization have also been investigated on the basis of the Laviron theory.

Finally, we will discuss the potentialities of a simple label free DNA hybridization detection method based on the specific ac voltammetric response of adsorbed cationic metal complex on the PNA–DNA duplex after hybridization by resorting to the analysis of the 23S rRNA gene of *Helicobacter pylori*.

*Present address : Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, UNITED KINGDOM

Nanomaterials at interfaces – an 18-year long journey

Yuval Golan

Department of Materials Engineering and
Ilse Katz Institute for Nanoscale Science and Technology,
Ben-Gurion University, Beer-Sheva, Israel 84105

Semiconductor nanostructures have attracted interest for reasons such as anisotropy of material properties via shape control, size-dependent quantum confinement effects, and as building blocks in nanoscale devices. "Wet" chemical routes for synthesis of semiconductor nanostructures are straightforward and cost-effective and can result in highly uniform nanomaterials with precise size and shape control. Three synthesis methods will be presented, all in which interfacial processes play a major role. The first method takes advantage of the air-water interface in the presence of ultrathin polyconjugated organic films as a unique medium for synthesizing highly aligned nanoparticles of, e.g., PbS and CdS, and their assembly into ordered structures. The second technique will highlight highly uniform nanorods and nanowires of ZnS, CdS and ZnSe capped with alkylamine surfactants, and will focus on the role of the organic surfactants in controlling their structure and assembly into 2D and 3D super-structures. Finally, chemical bath deposition also offers a simple and versatile route for producing high quality PbSe and PbS thin films directly onto GaAs single crystal substrates without the use of organic ligand molecules. A wide range of microstructures is obtained, from nanocrystalline films to epitaxial single crystal films. Along with conventional in-house characterization techniques, *in-situ* techniques such as laser light scattering and small angle synchrotron x-ray diffraction are employed for monitoring growth and ordering in real time.

Conducting-Polymer/Metal Nano-Composites

J. Janata*, A. Saheb, J. A. Smith and M. Josowicz

* corresponding authors : School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400

Electrochemical preparation of uncapped metal nanoclusters ($d < 1-20$ nm) is interesting from the point of view of design of electrocatalytic materials and of new selective sensing layers. In case of Au the elementary process is a $3e$ reduction of $AuCl_4^-$ resulting in one atom of Au. The top-down approach leads to self-assembly of Au clusters to form multi-atom aggregates. The reasons for this “clustering have been examined” and a working hypothesis how to prevent it has been formulated. The genuine “nano-effect” has been observed for clusters smaller than 5 nm by measuring shift of binding energy of Au_{4f} line in XPS spectra. This shift is attributed to coulombically limited formation of the contact potential between Au and electronically conducting polyaniline matrix. Similar effect has been reported for Au nanoclusters deposited on TiO_2 , on MgO and on clusters formed in molecular beams. We have attempted to assemble gold clusters from the “bottom-up”, by precisely controlled “atom-by-atom,” deposition into the conducting polymer matrix. Both spectroscopic and electrochemical supporting evidence has been obtained for existence of such atomic nano-composites. This approach complements formation of Au clusters from the “top-down” approach, in which clusters of gold are formed under purely electrochemical control.

1. J.A. Smith, M. Josowicz and J. Janata, *J. Electrochem. Soc.*, 150, (2003) E384-388 “Polyaniline-Gold Nanocomposite System”
2. J. A. Smith, M. Josowicz, and J. Janata, “Gold/Polyaniline Composite: Part I Moving Electrochemical Interface, *Phys. Chem. Chem. Phys.*, 2005, 7, 3614 – 3618
3. J. Anthony Smith, M. Josowicz, J. Janata, Mark Engelhard and Don R. Baer “Gold/Polyaniline Composite: Part II Effect of Nanometer Size Clusters”, *Phys. Chem. Chem. Phys.*, 2005, 7, 3619 – 3625

Support from NSF CHE--0137391

Self- and directed assembly of functional nanoscale structures

Paul S. Weiss

Departments of Chemistry and Physics, The Pennsylvania State University, University Park, PA 16802-6300,
USA
stm@psu.edu, <http://www.nano.psu.edu/>

We use molecular design, tailored syntheses, intermolecular interactions and selective chemistry to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements of single or bundled molecules. Interactions within and between molecules can be designed, directed, measured, understood and exploited at unprecedented scales. We look at how these interactions influence the chemistry, dynamics, structure, electronic function and other properties. Such interactions can be used to advantage to form precise molecular assemblies, nanostructures, and patterns, and to control and to stabilize function. These nanostructures can be taken all the way down to atomic-scale precision or can be used at larger scales. We select and tailor molecules to choose the intermolecular interaction strengths and the structures formed within the films. We employ some of these approaches in directed assembly to enable bioselective and biospecific binding. We develop hybrid strategies to create chemical patterns down to the single-molecule scale.

TiO₂ nanotubes: electrochemical formation, properties, applications

Patrik Schmuki

Department of Materials Science, WW4,
University of Erlangen-Nuremberg, LKO, Martensstr.7, Erlangen, Germany;
*E-mail: schmuki@ww.uni-erlangen.de

The presentation will deal with self-organized, high aspect ratio titanium oxide nanotubes grown by simple but optimized anodization. Key to obtain highly defined tubes controlled electrochemical treatment of Ti in fluoride containing solutions. In general, the morphology of porous TiO₂ and of the tubular layers is affected strongly by the electrochemical parameters such as solution pH and anodization voltage. By optimizing the local electrochemical conditions within the tubes, layers consisting of highly ordered TiO₂ nanotubes with a length of several 100 micrometers can be grown on Ti surfaces. The diameters that can be obtained range from 20 nm to 200nm - typical wall thicknesses are in the range of 10-20 nm (1-3). Titanium dioxide is a highly functional material that has numerous interesting properties, for example, in solar energy conversion, catalysis of the decomposition of organic compounds (self-cleaning), wettability and biocompatibility. Therefore this simple approach to produce this highly defined nanoscopic form of TiO₂ bears a high potential for technological exploitation.

We have recently shown that the TiO₂ nanotubular structures show significant conversion efficiencies, when dye-sensitized (4), can be used as a matrix for hydroxyapatite formation to achieve osseointegration with bones (5), show extremely enhanced visible photoresponse after N-doping (6), can be used as a highly efficient photocatalyst (7) as a catalyst carrier for Pt/Ru nanoparticles for methanol electrooxidation (8) or as a template for Cu deposition (9). Further, they show ability to change their hydrophobic/hydrophilic behaviour (10) under illumination.

The presentation will address particularly the fabrication of free standing photoactive nanotube membranes (11) and size sensitive interactions of biological cells with the nanotubes surface (12).

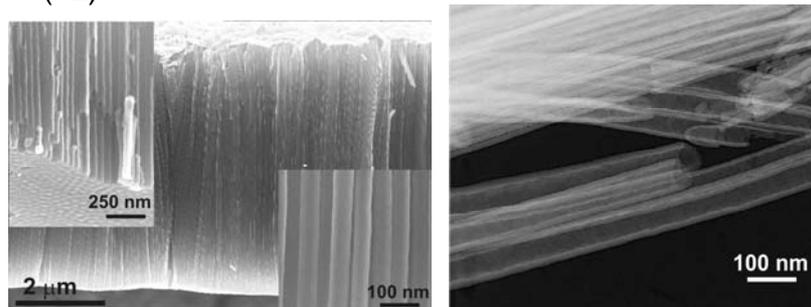


Figure 1. Example of self-organized TiO₂ nanotubular structure: SEM (a) and HRTEM (b). The insets in (a) show the tube walls and the layer bottom in detail.

1. J. M. Macak, H. Tsuchiya and P. Schmuki, *Angew. Chem. Int. Ed.*, **44**, 2100 (2005).
2. J. M. Macak, H. Tsuchiya, L. Taveira, S. Aldabergerova, P. Schmuki, *Angew. Chem. Int. Ed.*, **44**, 7463 (2005)
3. S. P. Albu, A. Ghicov, J. M. Macak, P. Schmuki, *phys. status solidi (RRL) - Rapid Research Letters* **1**, R65 (2007).
4. J.M. Macak, H. Tsuchiya, A. Ghicov, P. Schmuki, *Electrochem. Comm.*, **7**, 1133 (2005).
5. H. Tsuchiya, J.M. Macak, L. Mueller, J. Kunze, F. Mueller, P. Greil, S. Virtanen and P. Schmuki., *J. Biomed. Mater. Res*, **77A**, 534 (2006).
6. A. Ghicov, J.M. Macak, H. Tsuchiya, J. Kunze, V. Haeublein, S. Kleber, P. Schmuki, *Nano Letters*, **6**, 1080 (2006).
7. J. M. Macak, M. Zlamal, J. Krysa, P. Schmuki, *Small*, in press.
8. J. M. Macak et al., *Electrochem. Commun.*, **7**, 1417 (2005).
9. J. M. Macak, B. G. Gong, M. Hueppe, P. Schmuki *Adv. Mater.*, (2006) (in press)
10. E. Balaur, J.M. Macak, L. Taveira, P. Schmuki, *Electrochem. Comm.*, **7**, 1066 (2005).
11. S.P. Albu, A. Ghicov, J.M. Macak, R. Hahn, P. Schmuki, *Nano Lett.*, **7**, 1286 (2007)
12. J. Park, S. Bauer, K. von der Mark, P. Schmuki, *Nano Lett.* (2007) (in press)

Molecular self-assembly from active metals to carbon nanotubes surfaces

Zineb Mekhalif

Laboratoire de Chimie et d'Electrochimie des Surfaces, Facultés Universitaires Notre-Dame de la Paix, B-5000, Namur, Belgium
Zineb.Mekhalif@fundp.ac.be + 32.(0) 81.72.52.30

Two directions of the CES research dealing with the grafting of molecular connectors on surfaces will be presented. The first one focuses on the self-assembly of organic molecules on oxidisable metals while the second highlights the chemical functionalisation of carbon nanotubes (CNTs).

Although self-assemblies of organothiols on gold and copper have been extensively studied over the past years¹, less work has been reported on the more active metals such as nickel and zinc. In the first part, we will present our achievement in molecular functionalisation on copper, nickel and zinc by monolayer or multilayer assembly based on organothiol and organoselenol derivatives². Such systems are of particular interest since complicated structures can be designed and prepared with molecular precision and could offer new possibilities for technological applications using more common metals. We will particularly underline the critical effect of the surface chemical state and the way to control the interface favouring chemical and stable bond. Application of this research to electrical connectors will be shown as illustration³.

The second part will be devoted to CNTs functionalisation by chemical grafting of organosilane molecules. The control of this step influences significantly the dispersion process in liquids and in polymers matrices and furthermore the ultimate composite properties (electrical conductivity, mechanical properties, flame fire retarding...) ⁴ An example of an applied achievement shall be briefly reported ⁵.

[1] *Encyclopedia of Electrochemistry, Volume 10, Modified Electrodes* by Allen J. Bard, Martin Stratmann, Israel Rubinstein, and Masamichi Fujihira, James F. Rusling, Wiley, January 2007., Love J. C.r; Estroff L. A.; Kriebel J. K.; Nuzzo R..G.; Whitesides G.M. *Chemical reviews* (2005), 105(4), 1103-69.

[2] Mekhalif, Z.; Riga, J.; Pireaux, J.-J.; Delhalle, J. *Langmuir* (1997), 13(8), 2285-2290. Mekhalif, Z.; Laffineur, F.; Couturier, N.; Delhalle, J. *Langmuir* (2003), 19(3), 637-645. Laffineur, F.; Auguste, D.; Plumier, F.; Pirlot, C.; Hevesi, L.; Delhalle, J.; Mekhalif, Z. *Langmuir* (2004), 20(8), 3240-3245.

[3] *Two-layerfluoroalkane-perfluoroether lubricant coatings for lubrication of electric contacts in automobiles and other vehicles, PATENT : FR 2839316 A1- 07 novembre 2003, WO 03/09/2914-13 novembre 2003.*

[4] Vast, L., Philippin, G., Fonseca, A., B.Nagy, J., Delhalle, J., Mekhalif, Z. *Nanotechnology*, (2004) 15, (7) 781-785., Vast, L., F. Laffineur, F., Delhalle, J., Fonseca, A., B.Nagy, J., Mekhalif, Z., *Journal of Nanoscience and Nanotechnology*, 7, (2007) in press

[5] *Nanocomposites, their manufacture and uses, PATENT : EP 02447039.5 – 20 mars 2002. WO 03/07/8315 A2- 25 septembre 2003*

Posters

Controlling supramolecular assembly by scanning electrochemical microscopy and surface coverage determination of functional molecules at molecular printboard by potential step chronoamperometric technique at SECM

Jatin K. Sinha[†], Christian A. Nijhuis[‡], Manon J. W. Ludden[‡], Carolina N. Kirchner[†], Gunther Wittstock^{†*}, Jurriaan Huskens^{‡*}, Bart Jan Ravoo^{‡*}, David N. Reinhoudt^{‡*}

[†] Carl von Ossietzky University of Oldenburg, Institute of Pure and Applied Chemistry and Biology of the Marine Environment, Oldenburg, Germany
Laboratory of Supramolecular Chemistry and Technology, SRO Nanofabrication & MESA⁺ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands,

Universität Oldenburg, Fakultät 5 / Physikalische Chemie, AG Wittstock, D-26111 Oldenburg, Germany, jatin.k.sinha@uni-oldenburg.de, carolina.nunes.kirchner@uni-oldenburg.de, gunther.wittstock@uni-oldenburg.de, Ph: +49-(0)441-798-3973, Fax: +49-(0)441-798-3979.
University of Twente, MESA+, TNW/SMCT, PO Box 217, 7500 AE Enschede, The Netherlands, c.a.nijhuis@utwente.nl, M.J.W.Ludden@tnw.utwente.nl, j.huskens@utwente.nl, b.j.ravoo@utwente.nl, d.n.reinhoudt@utwente.nl

Molecular printboards were formed by self-assembled monolayers (SAM) terminated by β -cyclodextrin (β CD). These layers can bind generation 3 ferrocene-terminated dendrimers and cytochrome *c*-streptavidin conjugates by multiple host-guest interaction. The system can be seen as a model system for building functional surfaces based on multiple non-covalent interactions. In this study we used scanning electrochemical microscopy (SECM) in different arrangements in order to image the layout of patterned SAMs with this system and to perform a local determination of the surface concentration.

The SECM investigation are based on oxidizing or reducing the redox-active surface-bound guest. Due to the limited availability of the guest on the surface, the conditions have to be tuned to be able to sense the guest by a "surface redox titration". This has been accomplished by using relatively high scan rates in imaging experiments or performing chronoamperometric pulse experiments at fixed position of the ultramicroelectrode (UME) probe. Since the oxidized (ferrocenyl) form of the dendrimers is not bound efficiently by the β CD units, the dendrimers are released from the surface after UME-induced oxidation. This process has been used for patterning molecular printboards in a sequential manner. For this an UME-generated oxidant leads to a local oxidation of the bound Fc dendrimers and their subsequent release from the surface. In a second experiment the inhomogeneous distribution of Fc unit on the surface could be demonstrated. The surface concentration determined in the pulse experiment correlate well with the determination by UV/Vis spectrometry.

The contribution discusses the requirements and potentials of this approach for nano-sized materials.

Structural analysis of lipid monolayers and bilayers on the surface of thin silica and titania films deposited on gold by means of PM IRRAS

Izabella Zawisza[†], Martina Nullmeier[†], Sabine Szunerits[‡], Rabah Boukherroub[§],
Gunther Wittstock[†]

[†] Carl von Ossietzky University of Oldenburg, Faculty of Mathematics and Science, Center of Interface Science (CIS), Department of Pure and Applied Chemistry and Institute of Chemistry and Biology of the Marine Environment, D-26111 Oldenburg, Germany.

[‡] Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (LEPMI), CNRS-INPG-UJF, 1130 rue de la piscine, BP 75, 38402 St. Martin d'Hères Cedex, France.

[§] Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (LEPMI), CNRS-INPG-UJF, 1130 rue de la piscine, BP 75, 38402 St. Martin d'Hères Cedex, France

* corresponding author : izabella.zawisza@uni-oldenburg.de.

Infrared reflection absorption spectroscopy (IRRAS) is widely used for studies of the structure of thin organized organic layers on surfaces reflecting the IR radiation, such as Au or Pt. Polarization modulation infrared reflection absorption spectroscopy (PM IRRAS) provides the necessary sensitivity to obtain spectra even from surfaces covered by a thin layer of aqueous electrolyte solutions and opens a route for obtaining structural information on the molecular level of self-assembled organic layer at material surfaces. However, the need for an IR-reflecting substrate has so far limited the applicability to noble metal surfaces excluding technologically important oxide surfaces. These surfaces are of large importance for implants materials, light conversion devices, sensors and possess a large importance to understand geochemical and biogeochemical processes on a molecular level. SiO₂ absorbs IR radiation below 1300 cm⁻¹ but otherwise SiO₂ and TiO₂ are transparent. Calculations show that if they are deposited in the form of thin (up to 90 nm thick) films on IR reflecting material such as gold, the enhancement of the electric field at the interface is comparable to that of Au alone, fulfilling the surface selection rules. This prediction has been experimentally verified for the first time using PM IRRAS on thin silicate oxide and TiO₂ films.

As a model application PM IRRAS is applied for structural analysis of mono- and bilayers of 1,2dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) deposited using the Langmuir-Blodgett and Langmuir-Schaeffer techniques on silicon oxide, titanium and gold surfaces. The CH stretching modes show that the hydrocarbon chains exist in liquid and gel phase depending on the surface pressure of the film transfer. The tilt of hydrocarbon chains, C=O bond in the ester group and CN bond in choline group are provided quantitatively. In the bottom leaflet of the lipid bilayer the dipole-dipole interaction between positively charged choline and the negatively charged silica surface influences the arrangement of the polar head groups of the lipid molecule at the interface. Lipid films formed on the Au|SiO₂, Au|Ti and Au surfaces show two-dimensional long range order. On the silicate and gold substrates of the same roughness lipid films show similar arrangement.

Formation of nanotube films by self-assembly

Árpád Szűcs^{†*}, Tibor Kósa[†], Rita Smajda[‡]

[†] Department of Physical Chemistry, University of Szeged.

[‡] Department of Applied and Environmental Chemistry, University of Szeged.

* corresponding author: H-6720 Szeged, Rerrich tér 1., Hungary; aszucs@chem.u-szeged.hu.

Formation of thin carbon nanotube (CNT) films was investigated on various surfaces. We applied simple solution casting to develop CNT modified electrodes. Mixtures of solvents (dimethyl formamide, ethanol, acetone, water) and different concentration of CNT were used, and small drops of these solutions were allowed to dry onto the surface. It was observed, that the film formation could proceed in two different ways. In the first one, precipitation of CNT occurred as the drop dried, but the resulted film was very heterogeneous, it did not cover the whole surface, only patches of CNT could be found. Under suitable conditions, however, very even films could be formed. In this case, no precipitation took place, instead, along the evaporation of the solvent, a thin films of CNT appeared on the surface of the solution, i.e., at the solution|air interface. They were floating there as small islands. As the drop dried, the islands met, developing a contiguous membrane on the surface. Actually this membrane shrunk to the substrate when the solvent was gone. It seemed that CNT samples, having amphiphilic character could act as surfactants forming membranes between polar and apolar phases. This membrane formed by self-assembly, and it did not depend on the actual substrate on which the drop was. So principally similar film could be made on any surface, it could be conductor, insulator, hydrophobic, hydrophilic, etc. Practically, however, the stability of the film after shrinking was determined by the adhesion to the substrate and the cohesion of the film. For instance, on gold the film was very fragile. Putting a drop of solvent was enough to break the films into flakes detached from the surface. On glassy carbon, or on Teflon the films were stable, washing the surface could not break or remove the films. We measured the resistance of the films formed from different mixtures, and followed the film formation on quartz crystal microbalance, too.

Acknowledgement: This work was supported by the grant: OTKA T046232.

Visualization of local catalyst activity towards oxygen reduction in HCl solution by means of RC-SECM

Artjom Maljus, Kathrin Eckhard, Michael Bron, Wolfgang Schuhmann

Anal. Chem. – Elektroanalytik & Sensorik, Ruhr-Universität Bochum, Universitätsstr.150,
NC 04/788, D-44801 Bochum; E-Mail: artjom_maljus@yahoo.de

In order to analyse local catalytic activity with high spatial resolution a transient redox competition mode of scanning electrochemical microscopy (RC-SECM) has been developed [1]. In a bi-potentiostatic experiment the SECM tip is positioned in close proximity to the surface of the catalyst modified sample. Both electrodes are polarised to reductively consume molecular oxygen. If the SECM tip is close enough to an active catalyst site, it will start to compete with the sample for the very same analyte in the gap between them. This leads to a noticeable tip current decrease over active sites of the sample. In order to avoid complete O_2 depletion a potential pulse profile is used for electrochemical oxygen generation prior to the competition detection. Highly dispersed electro-deposited spots of gold and platinum on glassy carbon as catalysts for reduction of molecular oxygen were investigated and successfully visualised in chloride free phosphate buffer (pH = 7) using RC-SECM [1]. However, visualisation of local catalytic activity of catalysts for oxygen reduction in chloride containing solutions at low pH has not been reported yet.

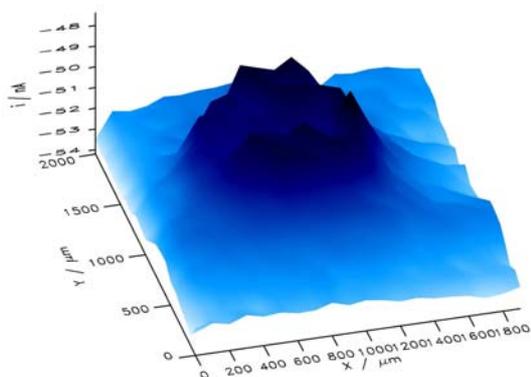


Figure 1. Local catalyst activity visualized by means of RC-SECM

In chloride containing solutions the oxygen generation pulse in RC-SECM leads to oxidation of chloride to chlorine. Here, cyclic voltammetry and chronoamperometry were used for investigation of the chloride oxidation process at Pt ultramicroelectrodes in HCl solution. To overcome chlorine evolution during SECM scanning for visualization of lateral catalyst activity the potential pulse profile was modified. However, simultaneously the oxygen evolution was prevented. By improving the pulse sequence the local catalytic activity of a model catalyst has been studied and successfully visualized in HCl solution (Fig. 1). Furthermore, a specifically designed electrochemical cell allows the investigation of powder catalysts. The

development of this approach and first results will be presented.

[1] K. Eckhard, X. Chen, F. Turcu, W. Schuhmann, *PCCP* **2006**, *8*, 5359-5365

Comparison of The Protective Properties 4-Nitrothiophenol and 4-Nitrobenzenediazonium Films Grafted on a ZnNi Coating Electrodeposited On Steel

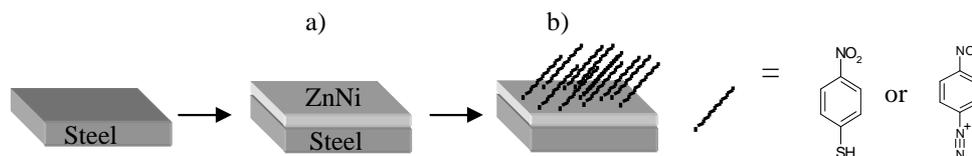
François Berger*, Joseph Delhalle, Zineb Mekhalif,

Laboratoire de Chimie et Electrochimie des Surfaces (CES), Facultés Universitaires Notre-Dame de la Paix (FUNDP), Rue de Bruxelles, 61, B-5000 Namur, Belgique

*francois.berger@fundp.ac.be

Sacrificial electrodeposited ZnNi is currently studied for replacing chromate conversion coatings (CCC) in anticorrosion applications. The present-day performances of ZnNi are still away from those of CCCs [1,2] and the additional organic layers cannot prevent the corrosive species to reach a metal surface completely. Suitable adhesion primers could improve the situation by minimizing the access of the corrosive species to the polymer/metal interface.

As a contribution to this interface problem, the present work provides a comparison of the protective properties of two structurally related molecules (4-nitrothiophenol and 4-nitrobenzenediazonium) (b) grafted on a ZnNi coating electrodeposited (a) on steel.



4-Nitrothiophenol films are prepared according to the self-assembly process already reported for semifluorinated alkanethiols SAMs on polycrystalline zinc [3]. Films of 4-nitrobenzenediazonium films have been obtained by cyclic voltammetry as mentioned in studies of Chaussé et al.[4].

The adsorption and the attachment of these molecules are characterized by X-ray Photoelectron Spectroscopy (XPS) and Polarisation Modulation-Infrared Reflection Spectroscopy (PM-IRRAS). The protective properties of the organic films against corrosion are investigated by linear sweep voltammetry (LSV), cyclic voltammetry (CV) and scanning vibrating electrode technique (SVET).

[1] Gavrilu, M.; Millet, J.P.; Mazille, H.; Marchandise, D.; Cuntz, J.M. *Surface and Coatings Technology* **2000**, 123, 164-172.

[2] Müller, C ; Sarret, M.; Garcia, E. *Corrosion Science* **2005**, 47, 307-321.

[3] Tortech, L. ; Mekhalif Z. ; Delhalle J. ; Guitard, F.; Geribaldi, S. *Thin Solid Films*, **2005**, 491, 253-259.

[4] Chaussé, A.; Chehimi, M.M.; Karsi, N.; Pinson, J.; Podvorica, F.; Vautrin-UI, C. *Chemistry of materials* **2005**, 14, 392-400.

Electroreduction of nitrate at copper electrodes and copper-PANI composite layers

J. Christophe¹, V. Tsakova², C. Buess-Herman¹

¹Service de Chimie Analytique et Chimie des Interfaces, (CHANI) – CP 255, Université Libre de Bruxelles, Bd. du Triomphe, 1050 Bruxelles (Belgium)

²Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl 11, 1113 Sofia, Bulgaria.

In the last years the electrochemical reduction of the nitrate ion was investigated with the purpose to find suitable methods for removal of nitrate from drinking water and waste solutions. Copper was found to be electroactive for the reduction of nitrate by promoting the first, rate-determining step of the reaction, i.e. the reduction of the nitrate ion to the nitrite ion.

In the present work we examine the electroreduction of nitrate ions at low concentration (5 mM) in acid and neutral aqueous solutions at polycrystalline copper electrodes, copper single crystals and at copper particles deposited in polyaniline (PANI) layers.

The reduction of nitrate is not significantly different on various copper atomic surface structures but is greatly dependent on the local pH at the electrode. By combining results from voltammetric measurements and electrolysis experiments, we show that NO_3^- is easily reduced to NH_4^+ in strong acidic solutions whereas the NO_3^- reduction in neutral solutions leads first to the formation of NO_2^- which is itself reduced at more negative potentials irrespective of the use of copper polycrystalline or single crystal electrodes. When copper particles are dispersed in polyaniline layers it is demonstrated that the electrocatalytic activity is strongly dependent on the way of depositing copper in the polymer layer. A clear difference is observed in the current response in absence and presence of nitrate ions for copper deposited in the reduced state of the PANI layer, whereas copper deposited in the oxidized state of the PANI layer remains still electrocatalytically rather inactive. Copper crystalline species act effectively for the investigated reaction only if copper conducting paths are available through the polymer matrix up to the underlying metal surface.

Bone growth development on a titanium oxide surface by combination of electrodeposition and molecular functionalization

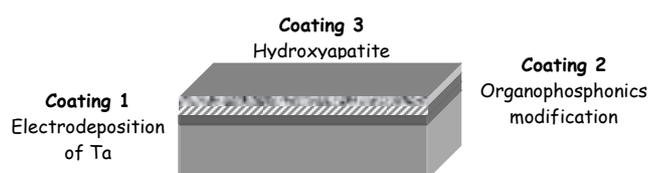
Christelle Arnould, Joseph Delhalle, Zineb Mekhalif

Laboratoire de Chimie et d'Electrochimie des Surfaces
Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium
* corresponding author : christelle.arnould@fundp.ac.be +32-(0)81.72.54.32

Due to their good biocompatibility, excellent mechanical properties, and high corrosion resistance, titanium and its alloys are widely used for dental and orthopaedic implants under load-bearing conditions. However, because they do not form strong chemical bonds with bone tissue, the possibility of 'loosening' over a long period may become a critical problem. As a matter of fact, titanium and its alloys have shown some corrosion and ions release in body fluids in the long term.

In this context the present paper deals with surface modification of the titanium oxide layer of a Ti substrate with two main objectives. The first one is the increase of corrosion resistance of the implant by forming a thin film of tantalum oxide (Ta_2O_5) on the titanium substrate. The second one is the improvement of hydroxyapatite nucleation and growth by modifying the Ta_2O_5 by organophosphonic molecules.

As shown on the figure, the surface modification occurs in three main steps and consists in the elaboration of different inorganic and organic coatings:



1. Electrodeposition of tantalum on the titanium oxide film of a Ti substrate.
2. Modification of the tantalum oxide coating by grafting organo-phosphonic acids.
3. Nucleation and growth of hydroxyapatite on the outermost layer of the system by immersion in a simulated body fluid.

The qualitative and quantitative observations as well as analysis of tantalum nucleation and growth of hydroxyapatite on the modified titanium substrate are performed using X-ray Photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM). Corrosion study is carried out with electrochemical techniques.

Kinetic studies of glucose oxidase embedded in polyelectrolyte multilayer films using scanning electrochemical microscopy (SECM)

Malte Burchardt [†], Gunther Wittstock ^{†*}

[†] Carl von Ossietzky University of Oldenburg – Faculty V – Department of Pure and Applied Chemistry and Institute for Chemistry and Biology of the Marine Environment

* corresponding author : D-26111 Oldenburg – gunther.wittstock@uni-oldenburg.de

Polyelectrolyte (PE) multilayer films containing glucose oxidase (GOx) were investigated by means of scanning electrochemical microscopy (SECM). Layer-by-layer deposition of positively charged poly(dimethyl diallyl ammonium chloride), PDDA, and negatively charged glucose oxidase, GOx, was used to create films with different number of enzyme layers and different film termination.

To obtain kinetic information about the embedded enzyme, approach curves with an SECM in the feedback mode have been recorded. With high glucose concentration and low mediator concentration, the complex reaction mechanism is simplified to a pseudo first-order reaction rate law. Comparison of experimental approach curves with working curves obtained from digital simulations by Mirkin et al. [1] leads to apparent reaction rate constants.

The influence of the concentration of the substrates glucose and ferrocinium methanol, the number of enzyme layers, the number of covering, inert PE layers and the time after preparation has been tested. The results indicate that in this system only the upper two layers of the film significantly take part in the reaction. Compared to GOx-terminated films, increased reaction rates could be observed for PDDA-terminated films. Scanning force microscopy revealed lower roughness of these films. Covering layers of inert PE hinder the mass transport from the solution to the enzyme.

[1] A. J. Bard, M. V. Mirkin, P. R. Unwin, D. O. Wipf, *J. Phys. Chem.* **1992**, 96, 1861

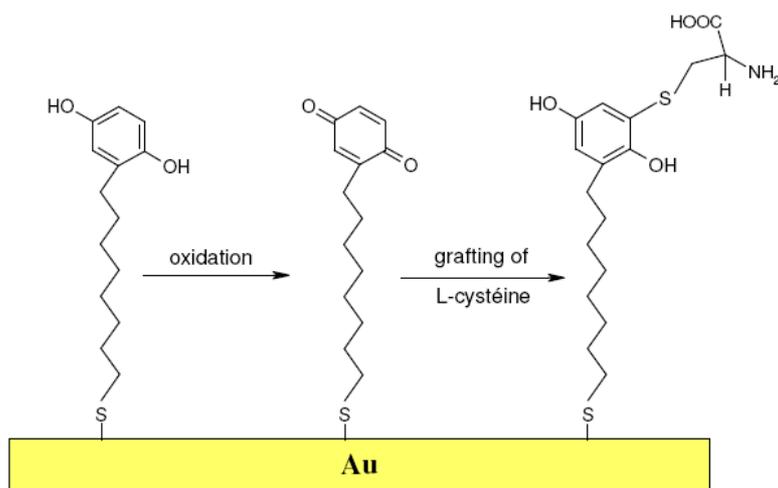
Hydroquinone terminated SAMs on gold as biosensor for cysteine

Emilie Delcourt, Claire Amato, Michel Prudent*, Hubert Girault*, Joseph Delhalle, Zineb Mekhalif

Laboratoire de Chimie et Electrochimie des Surfaces (CES), Faculté Universitaire Notre-Dame de la Paix (FUNDP), Rue de Bruxelles, 61, B-5000 Namur, Belgique

*Laboratoire d'Electrochimie Analytique et Physique, EPFL, Lausanne, Suisse
emilie.delcourt@fundp.ac.be

Cysteine plays an important role in glutathione metabolism. This amino acid is responsible for the antioxidant properties of glutathione and thus for the regulation of oxidant stress related to neuronal diseases (Alzheimer, Parkinson,...). In this field, the development of hydroquinone terminated alkanethiol SAMs on gold (111) for the immobilisation of cysteine derivatives, which will allow their further proportioning in the organism, is envisioned.



Synthesis of 2-(8-mercaptooctyl)benzene-1,4-thiol (H_2QH_8SH) and 8-(2,5-dihydroxyphenyl)octyl ethanethioate ($H_2QH_8SCOCH_3$) was achieved. Then formation of hydroquinone terminated SAMs on gold was realised in ethanol solution. The influence of terminal function (SH or $SCOCH_3$) chosen for the chemisorption of molecule to gold and the time of incubation (5h and 20h) have been compared.

SAMs organisation and composition were evaluated on the basis of spectroscopic measurements, such as Polarisation Modulation-Infra Red Reflection Adsorption Spectroscopy (PM-IRRAS) and X-ray Photoelectron Spectroscopy (XPS). Electrochemical Impedance Spectroscopy (EIS) was used to assess SAMs capacitance and resistance towards ionic penetration. Finally cyclic voltammetry was involved to oxidize terminal hydroquinone into quinone, allowing the grafting of cysteine. The presence of cysteine onto the SAMs was detected by XPS.

Electrochemical activity of platinum nanoparticles on gold and carbon substrates for oxygen reduction

N. Idrissi, C. Buess-Herman

Université Libre de Bruxelles, Service de Chimie Analytique et Chimie des Interfaces (CHANI), CP 255, Boulevard du Triomphe, B-1050 Brussels, Belgium.

Size and structural effects have remained central issues in electrocatalysis for already half a century. It is thus desirable to design electrode materials with high degree of controllability. The electrochemical dispersion of platinum particles onto a convenient substrate can be used to produce electrocatalysts with a high surface area and a high catalytic activity. Taking advantage of the stability of a golden substrate and the availability of a more common substrate such as carbon, platinum modified gold and platinum modified carbon can provide alternatives to bulk platinum electrodes for fuel cell application. The oxygen reduction reaction is of major importance to energy conversion, particularly in the field of fuel cells and metal-air batteries. The pronounced irreversibility of the oxygen reduction on most metal electrodes and the great number of possible pathways make the study of the reaction a real challenge. The situation is made more complicated by the sensitivity of the reaction rate to the state of the electrode surface.

Gold and carbon supported platinum electrocatalysts were prepared using a two-step procedure. The first step consists in depositing potentiostatically a bulk adlayer of copper. The second step is the open circuit displacement atoms by platinum, provided by an acidic solution of a hexachloroplatinate (IV) complex. Gold and carbon electrodes were also modified with electrodeposited platinum particles from the same complex solution.

The rotating disc and the rotating ring-disk techniques were used to study the kinetics of the oxygen reduction reaction on the modified electrodes. Morphologies of the nanosized platinum deposits are analyzed by Atomic Force Microscopy.

It was found that platinum modified gold electrodes show a higher catalytic activity in comparison with platinum carbon modified electrodes. Furthermore, we show that for the gold substrate the electrocatalytic activity depends on the copper deposition potential in the case of spontaneous dispersion and on the deposition potential platinum in the case of electrochemical dispersion of platinum. The activity increases with the overpotential. AFM measurements show that higher overpotential deposition lead to smaller particles and more homogeneously dispersed. The deposition potential can thus be used as a tool to tune the morphology of supported platinum.

Molecular self-assembly of alkaneselenols on copper

Grégory Fonder, François Berger, Balazs Csoka, Joseph Delhalle, Zineb Mekhalif

Laboratoire de Chimie et d'Electrochimie des Surfaces
Facultés Universitaires Notre-Dame de la Paix, 61 Rue de Bruxelles, Namur, Belgium
* corresponding author : gregory.fonder@fundp.ac.be +32-(0)81.72.54.32

Self-assembly of alkaneselenols on copper is part of our efforts towards the modification of active metal surfaces by organic molecules^{1,2}.

Compared to gold, the self-assembly of organothiols on copper faces the challenge of eliminating the superficial oxide layers. Previous studies carried out in our laboratory³ pointed out the need for suitable chemical and/or electrochemical pre-treatments to eliminate the metal (copper, nickel, zinc,...) oxide layers prior to reacting the organothiols with the surface to be modified. The goal of this work is to study the grafting mechanism of dodecaneselenol and its diselenide counterparts on electrodeposited copper. SAMs of *n*-dodecanethiol and its disulfide counterparts are similarly elaborated for comparison.

In a first step, we focus on the nature of the interfacial bonding, a critical parameter for the protection of copper against a potential reoxidation. In a second step, the formation of mixed monolayers (thiols, selenols) is attempted by trying out various modes of exchange reactions like partial electrochemical desorption and locally induced electrochemical desorption. Understanding these processes is a necessary step before undertaking a nano-structuration of the organically modified surface.

Characterizations of the SAMS are carried out using contact angles, XPS, ToF-SIMS, PM-IRRAS and infrared microscopy techniques in parallel with electrochemical studies (CV, SECM, SVET) .

[1] *Encyclopedia of Electrochemistry, Volume 10, Modified Electrodes* by Allen J. Bard, Martin Stratmann, Israel Rubinstein, and Masamichi Fujihira, James F. Rusling, Wiley, January 2007.

[2] Love J. C.; Estroff L. A.; Kriebel J. K.; Nuzzo R. G.; Whitesides G. M. *Chemical reviews* (2005), 105(4), 1103-69.

[3] Mekhalif, Z.; Riga, J.; Pireaux, J.-J.; Delhalle, J. *Langmuir* (1997), 13(8), 2285-2290. Mekhalif, Z.; Laffineur, F.; Couturier, N.; Delhalle, J. *Langmuir* (2003), 19(3), 637-645. Laffineur, F.; Auguste, D.; Plumier, F.; Pirlot, C.; Hevesi, L.; Delhalle, J.; Mekhalif, Z. *Langmuir* (2004), 20(8), 3240-3245.

Financial Support: Région Wallonne, FNRS

Investigation of glucose oxidase embedded in laterally structured polyelectrolyte multilayers

Malte Burchardt [†], Gunther Wittstock ^{†*}

[†] Carl von Ossietzky University of Oldenburg – Faculty V – Department of Pure and Applied Chemistry and Institute for Chemistry and Biology of the Marine Environment

* corresponding author : D-26111 Oldenburg – gunther.wittstock@uni-oldenburg.de

Layer-by-layer deposition of oppositely charged polyelectrolytes (PE) constitutes a versatile method to produce thin films [1]. Numerous materials such as polymers, small organic molecules, inorganic components, proteins, DNA, or colloids have been applied. Film thickness and properties can be changed precisely in a wide range by varying the number of deposited layers and deposition conditions, e. g. concentrations of PE, ionic strength, pH, and dipping time. Embedding enzymes into polyelectrolyte multilayer for bioreactor or biosensor applications has been proposed early [2]. Starting from surfaces which are only charged on certain areas, it is possible to build up localized polyelectrolyte multilayers[3].

The topic of this work is the fabrication and characterization of patterned PE multilayers containing glucose oxidase. Locally charged surfaces as primers were built by microcontact printing with carboxylic acid terminated alkane thiol on gold surfaces. To prevent unspecific adsorption of PE outside the charged areas, oligoethylene glycol terminated alkane thiol was used to fill the gaps. Alternate selective deposition of poly(dimethyl diallyl ammonium chloride), PDDA, and glucose oxidase, GOx, led to stepwise growth of micropatterned film.

The enzyme activity of these films was characterized using scanning electrochemical microscopy (SECM) in the generation collection mode. Mapping experiments were done to examine unspecific adsorption between the polyelectrolyte multilayers. The morphology of the microstructured polyelectrolyte multilayers as well as the quality of the alkane thiol monolayers were investigated with scanning force microscopy (SFM).

[1] G. Decher, *Science* **1997**, 277, 1232

[2] G. Decher, B. Lehr, K. Lowack, Y. Lvov, J. Schmitt, *Biosens. Bioelectron.* **1994**, 9, 677

[3] P. T. Hammond, G. M. Whitesides, *Macromolecules* **1995**, 28, 7569.

Elaboration by PVD of a WO₃ electrochromic coating

Charlotte Guisset[†], Fabrizio Maseri[‡], Zineb Mekhalif^{*†}, Joseph Delhalle[†]

[†] Laboratoire de Chimie et d'Electrochimie des Surfaces (CES), Rue de Bruxelles 61, 5000 NAMUR, Belgium.

[‡] Centre de Recherche et développement Arcelor, Boulevard de Colonster 57, 4000 Liège, Belgium.

* corresponding author: zineb.mekhalif@fundp.ac.be

A lot of work has been done on electrochromism. Tungsten trioxide is the most study composite amongst the materials that have this interesting property. Techniques like CVD, sol-gel are used to produce such compound but other deposit technique exists. Sputtering is a very interesting one which allows having high deposit rate and an easy control of the stoichiometry.

The goal of this work is the elaboration of an electrochromic display with tungsten trioxide synthesized by sputtering DC magnetron and deposited on ITO (indium oxide doped with tin). The influence on the optical properties of the films of the unbalanced and balanced mode will be studied.

The films are analysed by RBS (Rutherford Backscattering Spectroscopy), XPS (X-ray photoelectron Spectroscopy), DRX (X-ray diffraction) and X-ray fluorescence. The optical properties are analysed by ellipsometry.

The last step of this work consists of the insertion of lithium (with a solution of lithium perchlorate and propylene carbonate) in the lattices of tungsten oxide by cyclic voltamperometry.

Voltammetric determination of phenol using composite materials based on metal hexacyanoferrates and conducting polymers

Cecilia Lete ^{†*}, Stelian Lupu[‡], Mariana Marin [†], Nicolae Totir[†]

[†] Institute of Physical Chemistry "Ilie Murgulescu", clete@chimfiz.icf.ro

[‡] Department of Analytical Chemistry, Faculty of Applied Chemistry and Materials Science, University of Politehnica of Bucharest, Polizu Street 1-3, 011061, Bucharest, Romania

* corresponding authors : Cecilia Lete, Splaiul Independentei 202, Bucharest, Romania, clete@chimfiz.icf.ro

Conducting polymers such as azulenes have been extensively investigated owing to their electrochemical and optical properties and modified electrodes development. Another modifier that has attracted a great interest is iron (III) hexacyanoferrate (II), known as Prussian blue (PB). In the present work, bilayer modified electrodes containing PB and azulene, 2-[(E)-2-azulene-1-ylvinyl] thiophene have been prepared by electrochemical methods in various configurations onto Pt substrate. The Pt/PB/PAZ electrode has been obtained by electrodeposition of PB onto Pt electrode and thereafter the PAZ film has been electrogenerated on top of the Pt/PB modified electrode. The same procedure has been used for the Pt/PAZ/PB electrode an inner PAZ film was firstly deposited onto Pt substrate and then the PB layer has been electrodeposited. After the deposition of the bilayer structures, the modified electrode were investigated by using cyclic voltammetry. The bilayer modified electrodes have been used in the study of phenol electrooxidation. From differential pulse voltammograms, an anodic peak at +0.3 V vs Ag/AgCl is observed. The anodic peak current increases linearly with the phenol concentration in the range from 0.3 mM to 1.1 mM. Therefore this anodic peak can be used for the quantitative determination of phenol.

Acknowledgments: The financial support from the Romanian Ministry of Education and Research through grant CEEX 2006 – 1143/25.07.2006 is gratefully acknowledged.

SECM screening and electrochemical characterization of metal-metal oxide catalyst

Jose L. Fernandez and Cynthia G. Zoski*

New Mexico State University, Department of Chemistry

* corresponding authors : New Mexico State University, Department of Chemistry, MSC 3C,
P.O. Box 30001, Las Cruces, NM 88003, czoski@nmsu.edu.

Recent investigations on oxygen reduction (*orr*) catalysts have been reported which show synergetic effects between two or more catalyst components. These effects are explained on the basis of different models. One of these models states that an efficient bi-functional catalyst would be able to efficiently cleave molecular oxygen onto one surface site and electrochemically reduce the cleaved oxygen atom into water on the second surface site.¹ On this basis, pure thermodynamic data and DFT calculations have led to the design of efficient non-platinum metal-alloy *orr* catalysts.^{1,2} Another bi-functional catalyst configuration that should be able to efficiently accomplish this task is a binary mixture of metal nanoparticles that have very anodic oxide reduction potentials (e.g. Au) in intimate contact with a stable reducible oxide (e.g. TiO_x).

Here we report the use of scanning electrochemical microscopy (SECM) in performing rapid *orr* activity screening of binary catalysts containing metal nanoparticles of Au or Pd or their oxides (AuO_x and PdO_x, respectively) dispersed in a metal oxide matrix such as TiO_x, RuO_x, SnO_x, MnO_x, MoO_x. Arrays of combinations of these components on glassy carbon plates were prepared by dispensing picoliter volumes of precursor solutions, inducing the precipitation of the hydrous oxides by a wet route (e.g. by addition of ammonium hydroxide solution) on each spot, and applying a thermal treatment ($600^{\circ}\text{C} \leq T \leq 70^{\circ}\text{C}$) under inert atmosphere. Thermal treatment causes the partial or total decomposition of the noble hydrous metal oxide into metal nanoparticles, leaving them in intimate contact with the remaining non-reduced metal oxide. Those compositions showing clear synergetic effects for the *orr* with respect to the pure noble metal were prepared as highly dispersed carbon black-supported catalysts in Nafion and deposited on glassy carbon rotating disk electrodes. They were electrochemically characterized by cyclic voltammetry, and the *orr* activity and stability of these materials were analyzed in O₂(1 atm)-saturated 0.5 M H₂SO₄ solutions by slow potentiodynamic scans.

¹ J.L. Fernández, D.A. Walsh, A.J. Bard, *J. Am. Chem. Soc.* **127** (2005) 357-365.

² J.L. Fernández, J.M. White, Y. Sun, W. Tang, G. Henkelman, A.J. Bard, *Langmuir*, **22** (2006) 10426-10431.

Addressable nanoelectrode membrane arrays: scanning electrochemical microscopy (SECM) characterization and applications in electrocatalysis

Jose L. Fernandez and Cynthia G. Zoski*

New Mexico State University, Department of Chemistry

* corresponding author : New Mexico State University, Department of Chemistry, MSC 3C,
P.O. Box 30001, Las Cruces, NM 88003, czoski@nmsu.edu.

Addressable nanoelectrode membrane arrays (ANEMAs) based on a gold-filled track-etched polycarbonate membrane have recently been reported¹. The track-etched polycarbonate membranes were filled using gold electroless deposition into the 30 nm diameter pores in the membrane. The Au-filled membrane was secured to a lithographically fabricated addressable ultramicroelectrode (UME) array patterned with 25 regularly spaced (100 μm center to center spacing) 10 μm diameter recessed Pt UMEs to create 25 microregions of 10 μm diameter nanoelectrode ensembles (NEEs) on the membrane. Electrical connection between the Au-filled template array and the lithographic UME platform array was achieved by potentiostatic electrodeposition of Au into each of the 25 recessed Pt UMEs on the UME array platform. A multiplexer unit capable of addressing 64 individual micro NEEs on an ANEMA was designed and used in the ANEMA experiments. The steady-state voltammetric behavior of reversible one-electron transfer model redox couples on each of the micro NEEs result in sigmoidal-shaped voltammograms which are reproducible across the ANEMA. The reproducibility of the steady-state current can be attributed to the overlapping hemispherical diffusion layers at the Au-filled nanopores of each 10 μm diameter NEE of a ANEMA. ANEMAs have advantages of high reproducibility, facile fabrication, multi-time reuse of lithographically fabricated UME arrays, steady-state behavior, and a unique NEE platform for investigations. Their characterization and applications in electrocatalysis at nanoparticles by scanning electrochemical microscopy (SECM) will be demonstrated.

¹C.G. Zoski, N. Yang, P. He, L. Berdondini, and M. Koudelka-Hep, "Addressable Nanoelectrode Membrane Arrays: Fabrication and Steady-State Behavior", *Anal. Chem.* 79(2007) 1474-1484.

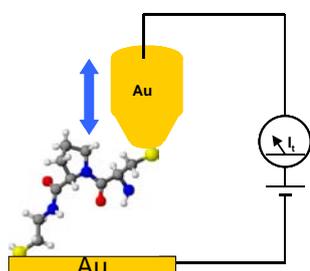
Measurements of single molecule conductance in self-assembled monolayers of oligopeptides

Elwira Maicka [†], Sławomir Sęk [†], Renata Bilewicz [†]

[†] *Warsaw University, Chemistry Department Pasteura 1, 02093 Warsaw, Poland*

* elmai@chem.uw.edu.pl

Self-assembled monolayers of alkanethiols with various terminal groups and oligopeptides on a gold surface are used as a model system for the study of long-range electron transfer ^{1, 2}. We synthesized a new molecule consisting of three-components cysteamine-proline-cysteine. The structure of the molecule allows changing the number of amino acids inside the chain by insertion of one or more proline units. Electron transmission through the peptides was measured using scanning tunnelling spectroscopy (STS). The molecular junctions were formed by trapping single molecules between the gold tip and the gold electrode. The conductance of the peptides depends on the molecule length and structure. By changing the components of the chain and terminal atom: sulphur or nitrogen, we could tune conductive properties of the molecules and assess the influence of the contacts on the electron transmission through that system.



1. Sęk S., Maicka E., Bilewicz R., "Efficient electron transfer through hydrogen bonded interface", *Electrochim. Acta*, 50 (2005) 4857.
2. Sęk S., Misicka A., Świątek K., Maicka E., "Conductance of α -Helical Peptides Trapped within Molecular Junctions", *Journal of Physical Chemistry B*, 110 (2006) 19671.

Construction of [60] fullerene-base three-dimensional architectures: towards the design of new optically active materials

Emerance Bietlot and Davide Bonifazi*

** Laboratoire de Chimie Organique des Matériaux Supramoléculaires (COMS)
Facultés Universitaires Notre-Dame de la Paix, B-5000 Namur (Belgium)
emerance.bietlot@fundp.ac.be*

In the past two decades, studies have been devoted to develop molecular donor–acceptor systems (triads, tetrad, pentads, etc.), which can mimic a cascade of electron-transfer steps of the natural photosynthetic reaction centers, leading to long-range charge separation with prolonged lifetimes. Specifically, fullerenes holds great promises as a spherical electron acceptor on account of the small reorganization energy during the electron transfer reaction processes. From their side, porphyrin photosensitizers are also suitable electron donating modules for efficient electron transfer because since they have been shown for feature small reorganization energies. In addition, rich and extensive absorption features of porphyrinoid systems guarantees increased absorption cross-sections and an efficient use of the solar spectrum. Thus, such a combination of chromophores (i.e., porphyrins and fullerenes) seems ideal for engineering light-harvesting chromophores throughout the solar spectrum that can ultimately lead to highly efficient photosynthetic reaction centers.

Preliminary results on the functionalization and preparation of novel carbon nanostructures containing fullerene derivatives will be here presented.

Sporopollenin as a naturally-selected molecular wire

Matthew THOMASSON [†], Grahame MACKENZIE [†], Stephen ATKIN [‡], Jay WADHAWAN ^{§*}

[†] Laboratory of Organic Chemistry, Department of Chemistry, The University of Hull, UK

[‡] The Hull York Medical School, The University of Hull, UK

[§] Laboratory of Analytical Chemistry, Department of Chemistry, The University of Hull, UK

* corresponding authors : Jay WADHAWAN, Department of Chemistry, The University of Hull, Cottingham Road, Kingston-upon-Hull HU6 7RX, United Kingdom; j.wadhawan@hull.ac.uk

The electrochemical interrogation of sporopollenin exines extracted from *Lycopodium clavatum* immobilised on graphite electrodes reveal the presence of hydroquinone-type functionalities sprinkled over the surface of each sporopollenin particle. Electron hopping transport between individual quinol moieties over the cupola-surface of the particles is computed to be highly rapid in acidic media, based on a spherical diffusion regime, and assuming the concerted proton transfer is not rate-limiting. It is suggested that the biological reason underpinning this form of natural selection is first to provide a physical and UV-shield, and second, to confer the sporopollenin particles with a “diffusional protection” of the valuable genetic information contained within sporopollenin against reactive oxygen species (or reactive nitrogen species) that would otherwise incur mutations within the haploid DNA.

Unbreakable solid-phase microextraction metallic Fibers

Isabelle Minet¹, Laszlo Hevesi², Manuel A. Azenha³, Joseph Delhalle¹, Zineb Mekhalif¹

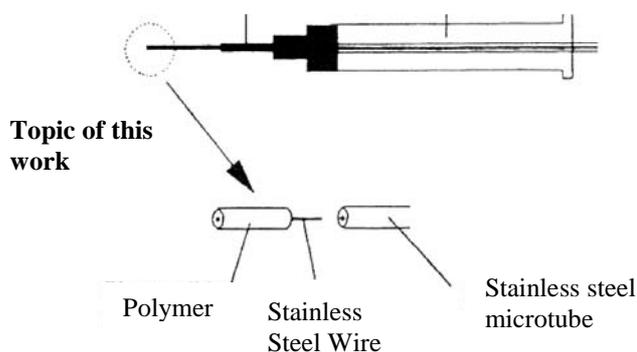
¹Laboratoire de Chimie et d'Electrochimie des Surfaces,²Laboratoire de Chimie des Matériaux Organiques
Facultés Universitaires Notre-Dame de la Paix, 61 Rue de Bruxelles, Namur, Belgium

³Chemistry Research Center, University of Porto, Rua do Campo Alegre 687, Porto, Portugal

* corresponding author : isabelle.minet@fundp.ac.be +32-(0)81-72.54.32

Solid-phase microextraction (SPME), a promising extraction technique developed in 1990 has been shown to be a simple and effective tool for the analysis of organic compounds from water samples^[1]. SPME exhibits many advantages over conventional sample preparation methods by integrating sample extraction, concentration and introduction to GC into a single step. Although the use of SPME fibers is increasingly gaining in popularity, they present a few drawbacks such as relatively low recommended operating temperature, their instability and swelling in organic solvents, the breakage of the fiber, the stripping of coatings and bending of the needle.

So, more robust SPME fibers with a long life and relative low cost are highly desired. In the present work, the polymer phase has been linked by covalent bonding to stainless steel wires.



A tethered diblock copolymer has been synthesized by sequential monomer addition to a self-assembled monolayer of (11-(2-bromo-2-methyl) propionyloxy)undecyl-phosphonic acid. Polystyrene-*b*-poly(methyl methacrylate)//stainless steel was prepared by the 'grafting from' method using atom transfer radical polymerization^[2,3]. The resulting diblock brushes were characterized by X-ray photoelectron spectroscopy (XPS), polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS), measurements of contact angle as well as scanning electron microscopy (SEM). Coupled with gas chromatography, the extraction of this new fiber is suitable for determination organic compounds in water with headspace^[4]. Experimental parameters such as adsorption and desorption conditions were studied.

[1] Pawliszyn, P. *Solid Phase Microextraction Theory and Practise*, Wiley-VCH, 1997

[2] Boyes, S.; Granville, A.; Baum, M. *Surface Science* 2004, 570, 1-12

[3] Zhao, B. *Polymer* 2003, 44, 4079-4083

[4] Azenha, M.; Nogueira, P.; Silva, F. *Anal.Chem.*, 2006, 78, 2071-2074

Gold nanoparticles modified with merocyanine 540 as a “smart” vehicle to target leukaemia cells

Michael BALL [†], Victoria COOPER [†], Louise EVANS [†], Robert SMITH [‡],
James DAVIS [‡], Nathan LAWRENCE [§], Jay WADHAWAN ^{†*}

[†] Laboratory of Analytical Chemistry, Department of Chemistry, The University of Hull, UK

[‡] Laboratory of Analytical Electrochemistry, School of Biomedical and Natural Sciences,
The Nottingham Trent University, UK

[§] Laboratory of Electrochemical Sensors, Schlumberger Cambridge Research, UK

* corresponding authors : Jay WADHAWAN: Department of Chemistry, The University of Hull, Cottingham Road, Kingston-upon-Hull HU6 7RX, United Kingdom. j.wadhawan@hull.ac.uk

Merocyanine 540 (MC540) is known to selectively accumulate in leukaemia cells, even in the presence of a vast excess of healthy cells. However, its fast photochemistry and photophysics means it is unable to be used as a tool in the optical distinction of leukaemia cells. In this poster, the electrochemistry of surfaces modified with MC540, and explore the feasibility of employing gold nanoparticles as a route to target leukaemia cells.

Electrochemical polymerization

Olivier SEGUT, Boris LAKARD, Guillaume HERLEM, Bernard FAHYS

I-UTINAM, CNRS-UMR 6213, Université de Franche-Comté, 16 route de Gray, 25030 Besançon Cedex, France, olivier.segut@univ-fcomte.fr

The research in the domain of chemically modified electrodes is very active since there is a need to develop well-defined surfaces to study the processes of electronic exchanges, and since these chemically modified electrodes have a strong active impact in some technologies looking toward the miniaturization of their systems. The reactions of electropolymerization offer a clean way to modify conducting surfaces. Indeed, these electrochemical reactions lead to the synthesis of polymer films with interesting and original properties by electronic transfer between the electrode and the monomer in solution in the double electrochemical layer.

If the history of electrodeposited polymer films begun with the discovery of polyaniline by Dall'Olio in 1968, polypyrrole by Diaz in 1979 and polythiophene by Garnier in 1986, electroactive aromatic polymer films have also been studied. Thus, our team has also contributed since 1997 to the discoveries of new reactions of electropolymerizations, especially those of linear polyethyleneimine (PEI-L) and linear polypropyleneimine (PPI-L) from non-aqueous amino electrolytes used as monomers (respectively ethylenediamine for PEI-L and 1,3-diaminopropane for PPI-L).

When reducing the modified electrodes sizes from the millimeter to the micrometer, their chemical behaviour seems to remain the same. Only the adhesion of the polymer films seems to decrease in a very meaningful manner. For example, the adhesion of polypyrrole is far more difficult on microsystems than on macro electrodes. That is why, we present in this study an original method permitting to avoid this problem.

Reference:

B. Lakard, G. Herlem, S. Lakard, R. Guyetant et B. Fahys, Polymer, 46, 12233-12239 (2006).

B. Lakard, G. Herlem, M. de Labachellerie, W. Daniau, G. Martin, J.C. Jeannot, L. Robert et B. Fahys, Biosensors and Bioelectronics, 19, 595-606 (2004).

B. Lakard, O. Segut, S. Lakard, G. Herlem et T. Gharbi, Sensors and Actuators B, 122, 101-108 (2007)

New Semifluorinated Dithiols Self-Assembled Monolayers as Oxidative Inhibitors of Copper Substrates

Sébastien Devillers^{1*}, Claire Amato¹, Patrick Calas², Joseph Delhalle¹,
Zineb Mekhalif¹

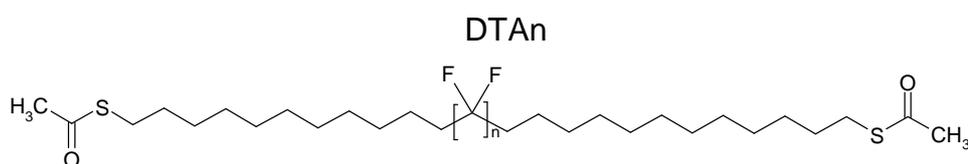
^{1†} Laboratoire de Chimie et Electrochimie des Surfaces (CES), Département de Chimie, Facultés
Universitaires Notre-Dame de la Paix, 61 rue de Bruxelles, B-5000 Namur, Belgium

² Institut Gerhardt, CMOS, UMR 5253, Université Montpellier II, 34095 Montpellier Cedex 05, France.
*corresponding author : sebastien.devillers@fundp.ac.be +32-(0)81-72.54.21

The efficiency of self-assembled monolayers (SAMs) of α,ω -semifluorinated dithiol and dithioacetate molecules as antioxidative coating treatments of copper surface are reported in this work.

New polyfluorinated dithiols HS-(CH₂)₁₁-(CF₂)_n-(CH₂)₁₁-SH called DTn, and corresponding dithioacetates CH₃COS-(CH₂)₁₁-(CF₂)_n-(CH₂)₁₁-SCOCH₃ called DTAn (n = 4, 6, 8) are used for self-assembly. SAMs of DTn and DTAn SAMs on both untreated copper and electrochemically reduced copper substrates are compared.

Composition and organization of the resulting monolayers have been studied by X-ray photoelectron spectroscopy (XPS) and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). Protecting properties of the resulting layers have been assessed by conventional electrochemical techniques, such as polarization curves and cyclic voltammetry.



Electrosynthesis and study of nanostructured molecular wires based on linear chains of coordinated rhodium atoms

F. Lafalet^{†*}, S. Chardon-Noblat[†], A. Deronzier[†], F. P. Pruchnik[‡], M. Rak[‡]

[†] Département de Chimie Moléculaire, UMR-5250 CNRS-Université Joseph Fourier, Grenoble, France

[‡] Faculty of Chemistry, University of Wrocław, Poland

*BP53, 38041 Grenoble cedex 09. frederic.lafolet@ujf-grenoble.fr

The strongly increasing demand for nanoscale molecular devices has given rise to an intense research activity in the area of low dimensional molecular solids and significant progress has been achieved during the last decade. The largest portion of literature covers organic molecules when organometallic molecular wires (MWs) have been rarely explored. Among new systems developed, those based on one-dimensional (1-D) polymetallic complexes appear to be very promising candidates for molecular electronics.

One of the main strategies for constructing such nano-scale wires involves a bottom-up approach using redox condensations of small molecular building blocks. One of the representative examples of this type of MWs, is the 1-D unsupported homo-valence metal chain complex $[M^0(L)(CO)_2]_n$ ($M = Ru$ or Os and $L =$ diimine ligands ; Fig. (a)).⁽¹⁾ We have developed an electrochemical method for tailoring thin films of such functionalized metal wires from suitable mono or binuclear coordination complexes. Recently, we have applied this electrochemical auto process to rhodium dimers, used as elemental building blocks, to synthesize rhodium infinite bonded chain complexes (Fig. (b)).⁽²⁾ We have demonstrated that this electrochemical process could be a powerful method to format such nanowires as thin films on conductive substrates.

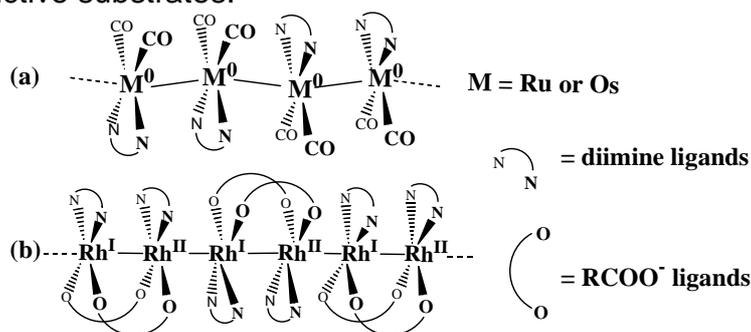


Figure: 1-D coordinated unsupported (a) and alternatively supported (b) polymetallic chains

We present here the electrochemical and the “conventional” chemical synthesis of 1-D mixed-valence multinuclear metal infinite redox chains $\{[Rh_2^{I,II}(L)_2(\mu-OOCR)_2]^+\}_n$. Characterizations, and properties of such molecular materials in solid state (redox, spectroscopic, magnetic and electric conductivity properties) and some outlooks about potential applications of these MWs will be given.

(1) S. Chardon-Noblat, A. Deronzier, R. Ziessel *A review Collect. Czech. Chem. Commun.* **2001**, 66, 207; N. Masciocchi, A. Sironi, S. Chardon-Noblat, A. Deronzier *Organomet.* **2002**, 21, 4009; F. Hartl, T. Mahabiersing, S. Chardon-Noblat, P. Da Costa, A. Deronzier, *Inorg. Chem.* **2004**, 43, 7250

(2) F. Lafalet, S. Chardon-Noblat, A. Deronzier, F. P. Pruchnik, M. Rak *submitted paper 2006*

Heterogeneous distribution of reactivity on nanostructured metallic biomaterials: Scanning probe microscopy studies of Ti6Al4V

Sascha E. Pust[†], Dieter Scharnweber[‡], Stefan Baunack[§], Gunther Wittstock^{†,*}

[†] Carl von Ossietzky University of Oldenburg, Faculty of Mathematics and Science, Center of Interface Science (CIS), Department of Pure and Applied Chemistry and Institute of Chemistry and Biology of the Marine Environment, D-26111 Oldenburg, Germany.

[‡] Technische Universität Dresden, Institute of Materials Science, Max Bergmann Center of Biomaterials, D-01062 Dresden, Germany.

[§] IFW Dresden, Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, P. O. Box 270016, D-01171 Dresden, Germany.

* corresponding author : gunther.wittstock@uni-oldenburg.de.

The biphasic ($\alpha+\beta$) alloy Ti6Al4V is predominantly in use for load-bearing joint implants because of its superior mechanical properties compared to pure titanium.^[1] Its use is based on the formation of a heterogeneously composed, *n*-semiconducting oxide layer that forms instantaneously in air and diminishes the release of potentially toxic ions into the surrounding tissue. Possible reasons for immunological rejection mechanisms are often connected to the electrochemical properties of this passive film.^[1] Therefore, a profound knowledge about its electrochemistry is of great interest.

The biphasic structure of the alloy results from a self-assembly that occurs when cooling the molten alloy. The size of the phase areas thereby depends on the conditions during the preparation process and may range from nanometers to micrometers. On coarse grained model samples with known grain orientation, we were able to determine the heterogeneous composition of the passive film on Ti6Al4V with Auger electron spectroscopy.^[2] Furthermore, scanning electrochemical microscopy (SECM) in feedback mode was applied to image the local reactivity of the oxide layer with high lateral resolution.^[3] The use of a broad range of redox mediators with different formal potentials allowed us to study the local electron transfer kinetics of the passive film and to relate the results to the semiconductivity of the oxide, opening up a route to the determination of local flat band potentials.^[2, 3] The results show that SECM is a powerful tool for the quantitative investigation of the local electrochemical behavior of nanostructured metallic biomaterials and may contribute to the improvement of their biocompatibility.

[1] D. Scharnweber, R. Beutner, S. Rößler, H. Worch, *J. Mater. Sci. Mater. Med.* **2002**, 13, 1215.

[2] S. E. Pust, D. Scharnweber, S. Baunack, G. Wittstock, *J. Electrochem. Soc.* **2007**, in press.

[3] S. E. Pust, D. Scharnweber, C. Nunes Kirchner, G. Wittstock, *Adv. Mater.* **2007**, 19, 878.

Chemically modified magnetic nanoparticules for protein selective isolation

Joël Lyskawa ^{*†}, Etienne Rousseau-Rogue [†], Olivia Guerre [†] and Christian Rolando [†]

[†] Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France

^{*} corresponding authors : LCOM - Laboratoire de Chimie Organique et Macromoléculaire - UMR 8009, UFR de Chimie, Université des Sciences et Technologies de Lille, Bâtiment C4, 59655 Villeneuve d'Ascq Cedex France. Email : joel.lyskawa@univ-lille1.fr

Chemically modified surfaces have known a great interest in the past years and it is more recently that they have started to be engaged in the improvement of protein separation. The major drawback of classical proteomic analyses is based on the multiple steps for the protein separation which lead to the loss or contamination of the sample. Thus, the use of modified surfaces seems very attractive to circumvent this problem.

In this poster, we report on the synthesis of magnetic nanoparticules functionalized by brush polymers which exhibit protein separation properties. These modified surfaces are fast and very straightforward systems for separation processes since they can easily remove proteins from a solvent or a biological environment by application of a magnetic field, with a magnet for example.

For this purpose, a functionalized monolayer was first immobilized on the nanoparticle surface (Fe_3O_4 magnetic beads). The latter contains specific functionalities which allow the initiation of an ATRP (Atom Transfer Radical Polymerisation) polymerization process. The main advantage of this "living" polymerization type is based on the potentiality of using a large range of functionalized vinylic monomers. The proof and the efficiency of the chemical modification were investigated by several surface spectroscopic techniques such as X-ray Photoelectron spectroscopy (XPS), ATR FT Infrared spectroscopy and Scanning electron Microscopy (SEM). Then, it will be possible to selectively isolate a unique class of protein from its original environment. This selectivity intrinsically depends on the specific chemical functionality introduced in the polymer on the surface. We will thus be able to selectively isolate hydrophobic proteins from their environment by using lauryl methacrylate (LMA) as monomer for the polymerization, glycoproteins when monomers containing a boronic function are employed or phosphopeptides with the use of IMAC type functionalities. For the latter, we used reactive GMA (Glycidyl methacrylate) monomers, on which IDA (iminodiacetic acid) moieties for metal chelating are introduced, followed by metal ions (Fe^{3+}). Other functionalized monomers for protein selective isolation are going to be investigated in our laboratory.

Finally, the efficiency of the chemically modified Nanoparticules as well the isolated protein characterization is achieved by MALDI-TOF mass spectroscopy. This new technology will be soon applied to the selective isolation of constitutive blood proteins.

Mixed polyfluorinated aminoterminated SAMs as new platform for biosensing

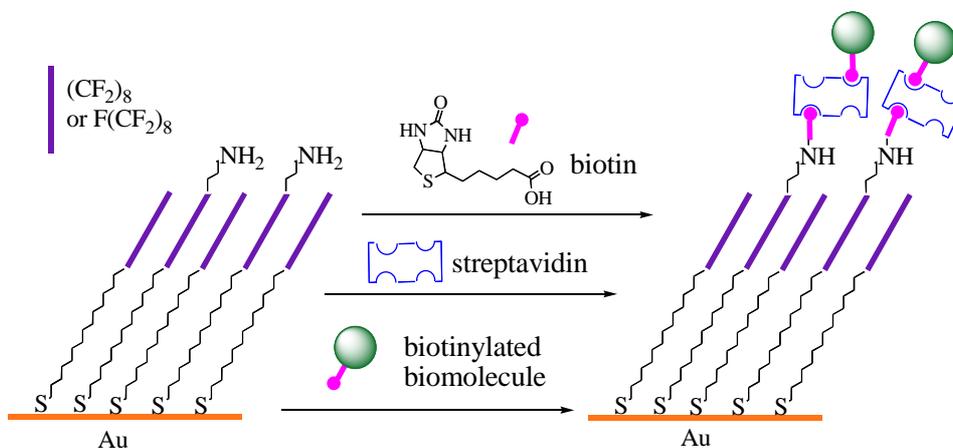
Claire Amato^{1*}, Cédric Volcke², Takashi Kakiuchi³, Joseph Delhalle¹, Zineb Mekhalif¹, Patrick Calas⁴

¹ Laboratoire de Chimie et Electrochimie des Surfaces (CES), ² Laboratoire de Spectroscopie Moléculaire de Surface (LASMOS),
Faculté Universitaire Notre-Dame de la Paix (FUNDP), Rue de Bruxelles, 61, B-5000 Namur, Belgique

³ Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University,
Japan

⁴ Charles Gerhardt Institute, CMOS, UMR 5253, Montpellier II University, France
corresponding author : amato.claire@fundp.ac.be +32-(0)81-72.54.21

Thin organic layers on solid surfaces have been extensively employed to mimic structures, interfacial phenomena, and processes. One way to prepare such layers is to utilize spontaneous chemisorption of long-chain organosulfur compounds from dilute solutions onto gold forming a so-called self-assembled monolayer (SAM). Thereby, functional organosulfur SAMs can find applications in chemically demanding environments, as well as for studies of complex interactions occurring at biological interfaces. Non-specific adsorption of biomolecules onto solid surfaces is a critical issue that must be carefully addressed. The use of high-molecular weight poly(ethylene glycol)¹, to obtain protein- and cell-repulsive properties is well known. Monolayer effective candidates in the search of surfaces resisting non-specific adsorption of proteins are numerous.



We planned to realise mixed polyfluorinated SAMs exhibiting terminal functions of biological interest and to test their properties as protein resistant surfaces. Results are presented including the synthesis of the original aminopolyfluoroalkanethiol², the study of their arrangement as mixed SAMs by Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), Polarisation Modulation-Infra Red Reflection (PM-IRRAS), X-ray Photoelectron Spectroscopy (XPS) and the evaluation of anti-non-specific adsorption properties by Atomic Force Microscopy (AFM).

¹ M. Riepl, K. Enander, B. Liedberg, M. Schäferling, M. Kruschina, F. Ortigao, *Langmuir*, 18, **2002**, 7016-7023. ² C. Amato, P. Calas, *J. Fluorine Chem.*, 124, **2003**, 169-175.

Preparation and characterizations of highly nanostructured porous templates obtained by self-assembly of the anodic aluminium oxides

François LE COZ, Laurent ARURAUULT *

CIRIMAT-LCMIE / Institut Carnot, Université Paul-Sabatier,

* CIRIMAT-LCMIE / Institut Carnot, Université Paul-Sabatier
118 route de Narbonne, 31062 Toulouse cedex 9, France
arurault@chimie.ups-tlse.fr ; phone: +33 (0) 561 556 148 ; fax: +33(0) 561 556 163

The porous anodizing of aluminium is a well-established process, widely used in different industrial fields like aeronautic, architectural decoration or anti-corrosive protection.... In 1953, Keller proposed an academic model of the Anodic Aluminium Oxide (AAO) porous film, based on a set of basic nanocells, each one including a pore. About twenty years ago, there was a renewal of interest for this process due to the possibility to observe experimentally this nanoporosity inside the anodic film using techniques such as FEG-SEM, TEM or AFM. Furthermore, the innovative research works of Masuda and Gösele, showed that it is possible, under particular operational conditions of anodizing, to obtain highly nanostructured templates by a self-assembly phenomenon.

But in spite of an increasing number of academic studies, the anodic film growth in general, and the self-organization of the nanoporosity in particular, are still considered as complex phenomena, depending on many experimental parameters. For example, previous experimental studies showed that the porosity and the chemical composition of the anodic film directly depend for a part on the aluminium substrate and on the anodizing electrolyte. But all the previous chemical analysis considered the anodic film only from a global point of view, higher than the micrometer level.

The aim of our research work was on the one hand to establish the correlations between the preparation parameters and the final characteristics of the AAO templates, and on the other hand to chemically characterize these templates, but at the nanoscopic scale of a basic cell, constituting the porous anodic film.

At first, we prepared AAO templates with different structures, from the "honeycomb" geometry (circular pores hexagonally ordered) to the "wasps nest" geometry (hexagonal pores hexagonally ordered). The influences of the pre-treatment steps of the aluminium substrate (polishing, annealing) on its surface properties and on the template characteristics, were particularly studied.

Secondly, these structures were then extensively characterized by TG-DTA, XRD, IRS, as well as by micro and nanoscopic techniques like EPMA, FEG-SEM, TEM-EDS. These analyses allowed to identify the chemical compounds and to evaluate its contents in the different parts of the basic nanocell. Finally, the various models of the porous anodic films growth were discussed on the basis of these results, contributing to a better understanding of the AAO templates preparation and of the self-nanostructuring phenomenon.

Self-assembled monolayers as components of nanomaterials

L. M. Abrantes [†], A. S. Viana [‡]

[†] CQB, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa

[‡] Laboratório de SPM, Faculdade de Ciências da Universidade de Lisboa

* corresponding author : Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, campo Grande, 1749-016, Lisboa, Portugal; luisa.abrantes@fc.ul.pt

Self-assembled monolayers (SAMs) are nanostructured organic materials, which adsorb strongly to metallic surfaces and comprise a number of valuable properties well suited for their general use in any nanoscience field. Due to their versatility, SAMs can be chemically tailored in order to design almost any surface at a nanometer level, bearing the appropriate functional groups for a given application [1].

The aim of this work is to illustrate the use of distinct SAMs, all based in the strong affinity of thiols, disulphides or lipoic acids towards gold surfaces, as suitable platforms for biosensing, electrocatalytic reactions and photoelectrochemical purposes [2-4].

In the first case, mixed SAMs of carboxylic and alkyl terminated thiols in combination with a detergent have been successfully used in the development of immunosensors of human Immunoglobulin G, where the non-specific interactions were greatly reduced. Modified gold with self assembled N-hydroxysuccinimide-ester disulphide has been prepared for the direct covalent linkage of Laccase. The bio-activity of the enzymatic surface was demonstrated for ABTS.

For the electrocatalytic applications, vitamin B₁₂ and metalloporphyrins were also immobilised on gold via self-assembly of specially designed derivatives and the modified surfaces display interesting catalytic activity, namely towards the reduction of molecular oxygen.

With the view of preparing hierarchical nanostructures of donor-acceptor dyads, fullerene SAMs were employed and the distribution of the large moieties on the surface have been investigated through the use of mixed SAMs.

All the above mentioned modified electrodes revealed to be stable and adequate for characterisation by a number of techniques, such as electrochemical methods, ellipsometry and scanning probe microscopy.

[1] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.*, 105 (2005) 1103.

[2] J. F. Cabrita, L. M. Abrantes, A. S. Viana, *Electrochimica Acta*, 50 (2005) 2117.

[3] Z.-H. Wang, A. S. Viana, G. Jin, L. M. Abrantes, *Bioelectrochemistry*, 69 (2006) 180.

[4] A. S. Viana, S. Leupold, F.-P. Montforts and L. M. Abrantes, *Electrochimica Acta*, 50 (2005) 2807-2813.

Electrochemical formation of nanoscale oxide powders in molten salts

Yolshina L.A.

Institute of High-Temperature Electrochemistry, Urals Branch of Russian Academy of Sciences
Kovalevskaya str.22, Ekaterinburg, 620219, Russia, , yolshina@ihte.uran.ru

Anodic oxidation of metals such as aluminum, titanium, zirconium and tantalum in molten chloride-nitrate bath at temperatures more than 800 K leads to formation on metallic surfaces dense defensive oxide films with good adhesion. The thickness of such covering is varying in the limits 5 nm to 20 μm .

If nitrate content is more than some limit value for each metal a lot of ultra-micro-dispersed oxide powders are presented in the salt electrolyte bulk. So as all salts and products of reaction are soluble in water one can obtain pure oxide powders after water solution and drying. Average size of oxide particles are 70-200 nanometers.

Metal oxidation in the salt melts with oxygen-containing anions remains one of the most simple and the most effective methods of high-temperature synthesis of oxides. It was carried out numerous investigations on passivation of metallic surfaces by oxide coatings which were formed because direct interaction of metal with oxide ions in the salt molten bath. Last years oxide synthesis science develops in two ways: formation of ultra-thin layers and ultra-disperse powders. The most interest is connected with the synthesis of thin layers and nano-powders of valve metals oxide such as Al_2O_3 , TiO_2 , Ta_2O_5 and zirconium dioxide ZrO_2 . Such oxide layers obtain high dielectric properties and can be used in supercapacitors, fuel cells and in computer device.

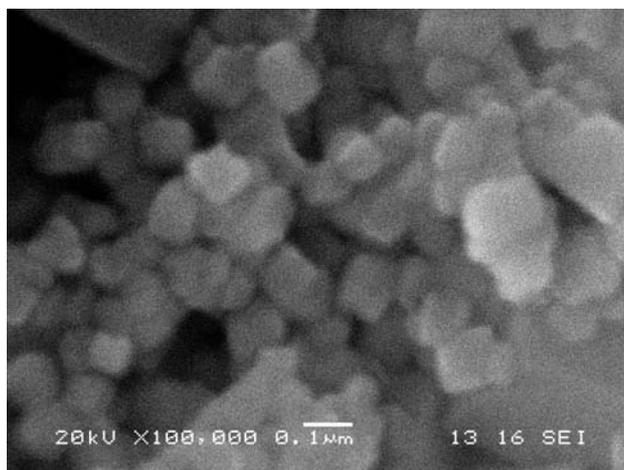


Figure. Surface image of Ta_2O_5 powder

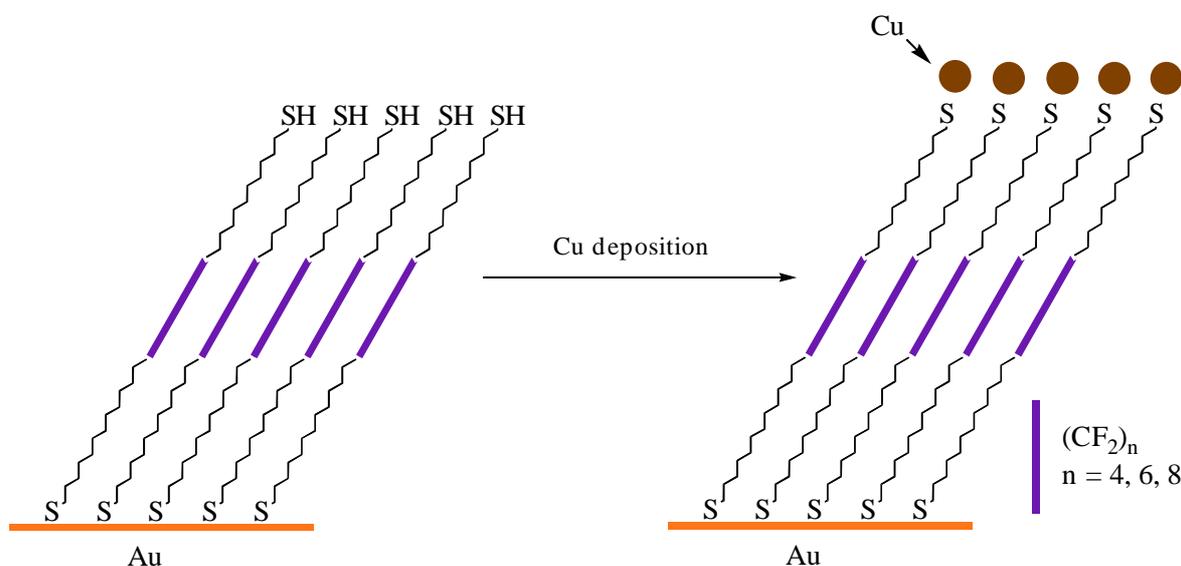
Functionalized gold surfaces of polyfluorinated dithiols for MMM Junctions

Claire Amato, Patrick Calas⁺, Joseph Delhalle, Zineb Mekhalif

Laboratoire de Chimie et Electrochimie des Surfaces (CES), Faculté Universitaire Notre-Dame de la Paix (FUNDP), Rue de Bruxelles, 61, B-5000 Namur, Belgique

⁺ Charles Gerhardt Institute, CMOS, UMR 5253, Montpellier II University, France
claire.amato@fundp.ac.be +32-(0)81-72.54.21

To overcome the technological and physical limits of microelectronic devices, metal/molecule/metal (MMM) junctions are currently envisioned¹. According to the electronic properties of organic molecules used, these new molecular electronic components have found applications as molecular rectifier, molecular transistor, molecular switch or molecular memory. A bottom up approach to build MMM is to form a self-assembled monolayer (SAM) of difunctional molecules chemisorbed at their two ends onto two electrodes. Self-assembly of difunctional molecules is complicated by the fact that both terminal functional groups are reactive with the target substrate. To be involved in MMM junctions, only one functional group must bind to the substrate to allow further metallization on the terminal group located away from the surface.



Herein we present the self-assembly of polyfluorinated dithiol molecules onto gold surface. Their ability to bind gold substrate by only one terminal function per molecule is evaluated as a function of time of formation, solvent of incubation and length of perfluorinated segment.

Syntheses of difunctional polyfluoroalkane molecules are reported for the first time. The SAMs formation is studied by X-ray Photoelectron Spectroscopy (XPS), Polarisation Modulation-Infra Red Reflection (PM-IRRAS) and Electrochemical Impedance Spectroscopy (EIS).

Electrochemical DNA hybridization detection using the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ /DNA interactions by ac voltammetry

Marc Steichen, Claudine Buess-Herman

Service de Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles, Boulevard du Triomphe 2, CP 255, 1050 Bruxelles, Belgium

* corresponding author : Claudine Buess-Herman, email: cbuess@ulb.ac.be.

A label-free electrochemical DNA hybridization detection method based on the electrostatic interactions of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ cations with the anionic phosphate backbone of DNA is proposed. Cysteine-SH modified PNA probes are immobilized on the polycrystalline gold electrode as capture probes in a mixed self-assembled-monolayer with 4-mercaptobutan-1-ol (MCB). Peptide nucleic acids (PNA) are structural DNA analogues containing a neutral N-(2-aminoethyl)-glycine pseudopeptide backbone and show higher specificity for DNA recognition. The cationic ruthenium complexes do not interact electrostatically with the PNA probes due to the absence of the anionic phosphate groups before hybridization. After the PNA-DNA hybrid formation, $[\text{Ru}(\text{NH}_3)_6]^{3+}$ adsorbs on the anionic DNA backbone, giving a clear hybridization detection signal in the ac admittance voltammogram [1].

The analytical parameters (sensitivity, selectivity and reproducibility) are evaluated. The method is sufficiently selective to detect the two single-base mismatches A2143G and A2144G, internal to the 23S rRNA gene of *Helicobacter pylori* and responsible for more than 90% of antibiotic resistance to clarithromycin in ulcer and gastritis treatments. Moreover the system is successfully applied to the detection of complementary PCR fragments extracted and amplified from SS1 *H.pylori* strain.

The rate constants of the electron transfer kinetics of the $[\text{Ru}(\text{NH}_3)_6]^{3+}$ complex on the PNA modified electrode after DNA hybridization and the PNA probe surface density have been evaluated according to the Laviron theory [2].

The effect of the applied electrode potential on the hybridization process (electronic stringency) is investigated in order to optimize the discrimination against single-nucleotide polymorphism.

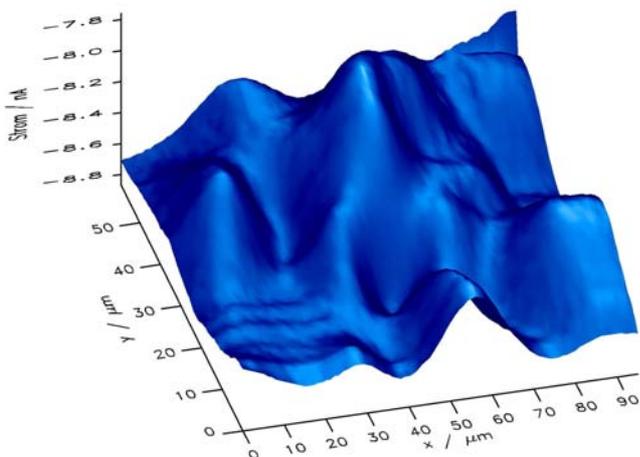
[1] M. Steichen, Y. Decrem, E. Godfroid and C. Buess-Herman, *Biosensors & Bioelectronics*, (2007), **22**, 2237-2243.
[2] E. Laviron, *Journal of Electroanalytical Chemistry*, (1979), **97**, 135-149.

Electrochemical characterisation of membranes coated with diamond-like carbon

Michaela Beckmann¹, Sebastian Neugebauer¹, Herbert Kieseles²,
Wolfgang Schuhmann¹

¹Anal. Chem. – Elektroanalytik & Sensorik;
Ruhr-Universität Bochum Universitätsstraße 150, 44780 Bochum
²Drägerwerk AG, Moislinger Allee 53-55, 23542 Lübeck
email:michaela.beckmann@rub.de

Diamond-like carbon (DLC) plays an important role in material science. Properties like high mechanical hardness, chemical inertness, low friction and wear coefficients and optical transparency lead to a wide spread application in e.g. machine elements, cutting and forming tools, in car industry and optics as well as protective and biomedical coatings [1-2]. Recently, the use of DLC films as electrode materials in gas sensors has evolved as a new application [3]. Although these coatings are already used in industrial applications, their electrochemical properties are not fully understood. Here, we use scanning electrochemical microscopy (SECM) in the feedback mode to locally elucidate electrochemical properties of DLC-coated Teflon membranes.



Visualisation of the electrochemical activity of the coated membrane

SECM enables the visualization of local electrochemical activity of a sample surface with high lateral resolution. In order to collect information about the electron transfer kinetic at a DLC coated porous Teflon membrane approach curves in the feedback mode of SECM have been recorded. Differences in the electron transfer kinetics have been detected depending on the used redox mediator. The electron transfer at the surface could be influenced by applying different potentials at the sample surface in a bi-potentiostatic experiment. In addition, the local activity of the sample has been visualized using SECM in the feedback mode in combination with constant-distance mode positioning using nanoelectrodes as SECM tips.

- [1] J. Robertson, 2002, *Mater. Sci. Eng. R* 37, 129-281
[2] A. Erdemir, C. Donnet, 2006, *J. Phys. D: Appl. Phys.* 39, R311-R327
[3] H. Kieseles, F. Mett, P. Tschuncky, DE 19939011C1

Localized desorption of self-assembled monolayers on copper surfaces

Balázs Csóka, Grégory Fonder, Joseph Delhalle, Zineb Mekhalif

Laboratoire de Chimie et d'Electrochimie des Surfaces
Facultés Universitaires Notre-Dame de la Paix, 61 Rue de Bruxelles, Namur, Belgium
* corresponding author : balazs.csoka@fundp.ac.be +32-(0)81-72.55.17

Organothiols form well structured, compact layers on noble metals (gold, silver ...) as well as on other metal surfaces like copper or nickel.¹⁻³ The formation and structure of these layers have been already investigated and by now well understood. Desorption processes were also studied by several research groups.²

Since the first report about Scanning Electrochemical Microscopy (SECM) by the Bard group, several studies have been published about the localized desorption of SAMs from gold surfaces.⁴ Because SECM gives a high precision distance setting from the sample surface, the desorption spots are well focused and have approximately the same size as the tip used. After desorption, the readsorption with other SAMs were also shown to produce biologically active functionalized spots on the surfaces.⁵

In this work we present examples of localized electrochemical desorption of SAMs layers from copper surfaces. The method shown here is more simple than the previously published ones and has many benefits compared to the "conventional" experiments. It also shows the possibility of producing multifunctional mixed monolayers.

The results on copper samples will also be compared with results of desorption of SAM on gold. The SECM results are supported by classical analytical experiments as well as infrared microscopic images.

[1] Ulman, A. *Chem. Rev.* (1996), 96, 1533.

[2] Azzaroni, O.; Vela, M.E.; Fonticelli, M.; Bentez, G.; Carro, P.; Blum, B.; Salvarezza, R.C. *J. Phys. Chem. B* (2003), 107, 13446-13454.

[3] Mekhalif, Z.; Riga, J.; Pireaux, J.-J.; Delhalle, J. *Langmuir* (1997), 13(8), 2285-2290. Mekhalif, Z.; Laffineur, F.; Couturier, N.; Delhalle, J. *Langmuir* (2003), 19(3), 637-645. Laffineur, F.; Auguste, D.; Plumier, F.; Pirlot, C.; Hevesi, L.; Delhalle, J.; Mekhalif, Z. *Langmuir* (2004), 20(8), 3240-3245.

[4] Uheil, J.; Boldt, F.M.; Börsch M.; Borgwarth K.; Heinze, J. *Bioelectrochem.* (2000), 52, 103-110.

[5] Wittstock, G.; Schuhmann, W. *Anal. Chem.* (1997), 69, 5059-5066.

Financial support:

Programme institutionnel des bourses de recherche post-doctorale FUNDP-CERUNA

Multilayer assemblies for light energy conversion

Mohamad Hojeij, Nicolas Eugster, Bin Su and Hubert Girault*

* Laboratory of physical and analytical electrochemistry, Institute of chemical sciences and engineering, Swiss Federal institute of technology in Lausanne, CH-1015, Lausanne, Switzerland

*Email: hubert.girault@epfl.ch, mohamad.hojeij@epfl.ch

In recent years, the fabrication of novel ultrathin film systems featuring multi-functionalities has been extensively studied because of their potential applications in electronics, photonics, sensors and photoelectrochemical cells. The goal of the present work was to develop film-modified electrodes for light energy conversion applications. Ultrathin polypeptide multilayer films are assembled by the electrostatic adsorption of alternating monolayer of poly-L-lysine and poly-L- glutamic acid onto carboxylic acid terminated alkanethiol-modified gold surfaces. These polypeptide multilayer films are hydrophilic, can bind electroactive anions such as ferri/ferrocyanide, and are stable when immersed in organic solvents such as 1,2-dichloroethane. Cadmium selenide (CdSe) quantum dots stabilised by citrate groups have been synthesised and characterized by UV-Vis spectroscopy and transmission electron microscopy. The CdSe QDs were electrostatically attached to the multilayer film assembly and used photoactive species. In order to increase the conversion efficiency of the system, 3-Dimensional nanostructures have been developed. Photocurrent responses originating from the CdSe sensitised ultrathin multilayer film were investigated as a function of the applied potential, the number of layers and the presence of a quencher in the organic phase. A theoretical model and simulations are proposed in order to rationalise the kinetics of the electron transfer and the photocurrent responses.

Fluorescence lifetime measurements using the time correlated single photon counting (TCSPC) technique were also used to study the non-linear fluorescence properties of CdSe QDs in solution and attached to the film.

Self-assembled monolayers/insulator/silicon based biosensing

Alexander Mottel¹, Hila Einati¹, Alexandra Inberg¹, Yelena Sverdlov¹ and Yosi Shacham-Diamand^{1,2}.

¹ Dept. of Physical Electronics, Eng. Faculty, and the Univ. Res. Inst. for Nano Science and Nano-Technologies, Tel-Aviv University, Ramat-Aviv 69978, Israel

² The Dept. of Applied Chemistry, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan,
Corresponding Author:Hila Einat, Email:einatihi@post.tau.ac.il

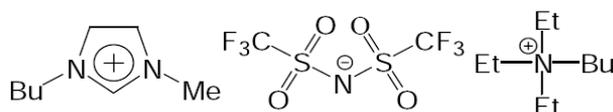
Self assembled monolayers (SAMs) using various organic molecules were constructed on thin thermal silicon dioxide on silicon structures for biosensing applications. The monolayers are part of a capacitor sensor based on the Electrolyte-Insulator-Silicon (EIS) structure. The main goal of this work is to investigate the ability of SAMs for acting as an intermediate layer between aqueous solutions and silicon based biosensors. This work presents monolayers based on tri-methoxy silanes with various functional groups such as: a. (3-Aminopropyl)-trimethoxysilane, b. Octadecyltrimethoxysilane and c. Trimethoxy(3,3,3-trifluoropropyl)silane. The biosensor is a differential sensor with a built in reference based on the structure of Electrolyte-Insulator-Silicon (EIS) or in Ion-Sensitive-Field-Effect-Transistors (ISFETs). While the methyl and fluorine groups act as the reference part, which is passive to the bio-molecules detection, the capacitor containing the amine groups has the sensing capabilities to the biological molecules. The amine (NH₂) tail groups were active for those attachments via glutaraldehyde. The film's study and characterization was made by Spectroscopic Ellipsometry, Contact Angle method (CA) and FT-IR spectroscopy. The electrical methods such as Capacitance-Voltage (C-V) and Electrochemical Impedance Spectroscopy (EIS) were used to investigate the whole Electrolyte/SAM/SiO₂/Si structure. We will show the detection capabilities of these 2D structures, its electrical equivalent model through a simulation fitting and will discuss the application of those structures to bio-sensitive MOS devices – both capacitors and MOS transistors.

Scanning electrochemical microscopy in non-usual solvents: the inequality of diffusion coefficients problem

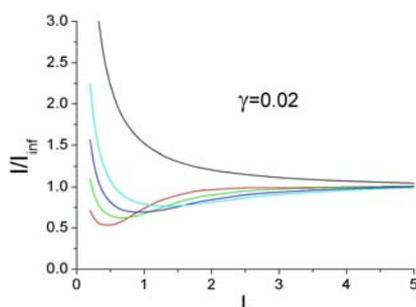
Jalal Ghilane, Philippe Hapiot,* Corinne Lagrost and Dodgi Zigah

Sciences Chimiques de Rennes (Equipe Macse). UMR CNRS – Université de Rennes 1 N° 6226. Campus de Beaulieu. 35042 Rennes Cedex.

Scanning Electrochemical Microscopy (SECM)¹ appears as a powerful tool for the local investigation of surfaces - interfaces in non usual solvents like room temperature ionic liquids (RTILs).² RTILs are ionic liquids (solvents that are exclusively composed of ions) that are liquid at room temperature and are good media for specific electrochemical experiments.³



Besides the expected difficulties arising from the higher viscosity of RTILs,^{3,4} the major problem comes from the inequality of the diffusion coefficients between the oxidized and reduced species of the redox mediator used to probe the interface. These inequalities lead to large anomalies in the current curves that in extreme cases, simply impede the recording of stationary approach curves.



Simulated apparent approach curves (positive feedback) . Effect of the experimental time.

Theoretical and specific aspects of the problem were treated by an extension of the model originally presented by Unwin *et al* that was adapted to the phenomena observed in ionic liquid.⁵ Conditions of applicability for recording steady state approach curves in ionic liquids and consequences of erroneous data treatment will be discussed. These discrepancies with the simple models (when diffusion coefficients have been taken as equal), can be transformed in a powerful method to characterize the transport properties of species dissolved in RTIL. The analysis is based on transient SECM experiments and easy determinations from non-ambiguous adimensional parameters.⁶

Experimental examples based on SECM in RTILs using common redox couples will be analyzed in view of the model. Reexamination of reactivity data, as those in previously published investigations by other electrochemical techniques, will also be discussed.^{4,6}

(1) "Scanning Electrochemical Microscopy"; Bard, A. J.; Mirkin, M. V., Eds.; Marcel Dekker: New York, 2001.

(2) Carano, M.; Bond, A.M. *Australian J. Chem.* 2007, 60, 29

(3) Sivester, D.S.; Compton, R.G. *Zeitschrift. Fur Phys. Chem.* 2006, 220, 1247 and ref. therein.

(4) Lagrost, C.; Preda, L.; Volanschi, E.; Hapiot, P. *J. Electroanal. Chem.* 2005, 1, 585.

(5) Martin, R.D.; Unwin, P.R. *J. Electroanal. Chem.* 1997, 439, 123.

(6) Ghilane, J.; Lagrost, C.; Hapiot, P. *Anal. Chem.* 2007, Submitted.

Organic photoactive layers derivatives of thiophene-carbazole for nanotechnology

Nicolas Berton^a, Julien Danet^a, Isabelle Fabre-Francke^{a,b}, Frédéric Chandézou^a, Saïd Sadki^a

a Laboratoire d'Electronique Moléculaire, Organique et Hybride (LEMOH)-SPRAM-UMR 5819 (CEA-CNRS-UJF)

CEA Grenoble-Département de Recherche Fondamentale -17 rue des Martyrs-38054 Grenoble cedex 9

b CEA-LETI-MINATEC

CEA Grenoble-Département de Recherche technologique -17 rue des Martyrs-38054 Grenoble cedex 9

*Prof Saïd Sadki : UMR5819-SprAM (CEA-CNRS-UJF), Structures et Propriétés d'Architectures Moléculaires Bâtiment C5 - Pièce 645 DRFMC, CEA Grenoble, 17 rue des Martyrs, 38054-Grenoble cedex 9, email : said.sadki@cea.fr

A great deal of attention has been focused on conjugated polymers due to the broad range of applications for which they are potentially useful¹. Photovoltaics devices, LED's, field effect transistors, electrochromics devices, and various types' sensors are under investigation by numerous researchers around the world. As such, the search for new functional and responsive conjugated polymers exhibiting electrochromism, photochromism or NLO properties are especially sought after for use in such applications as display technology or data storage. Preparation of conjugated photochromic polymers leads the development of original materials which are good candidates of optical switches and storage devices. In designing a photochromic conjugated polymer, several can be taken. In the simplest approach the photochrome can be attached as a pendant group to the polymer backbone through a nonconjugated linkage. In the second approach a fully conjugated polymer is synthesized in which the conjugation of the photochrome is continuous with the backbone by either incorporating the photochrome directly in the backbone or using a fully pendant group. Such fully conjugated polymers are especially interesting because of the possibility for a cooperative interaction between the polymer and the photochrome due to the continuous electronic conjugation¹. Because of their interesting physical properties under irradiation of their photochromic groups, molecules based of carbazole-anils and EDOT-carbazole-anils derivatives are investigated. Anils (salicylidenes-anilines) are interesting class of photochrome. The mechanism for the photochromism is based on a tautomerization. The enol form is colorless, but upon irradiation with UV light the colored keto form is produced². Optimized synthesis of anil-carbazole monomers in one pot permits to obtain some derivatives whose substituent effect were studied.

These monomers are deposited on a glass substrate as a solid film to be studied under irradiation. It is shown that the photochromic character of these molecular films is exalted by addition of tertibutyl groups on the phenolic ring. A reversible photo-commutation is then possible. Monomer CzAnil 1 and CzAnil 2 were electropolymerized by cyclic voltamperometry and chronopotentiometry in nitrobenzene TBAP 0.1 M. Conducting polymer films are obtained on platinum and ITO electrodes These new polymers films were electrochemically characterized by cyclic votamperometry in acetonitrile TBAP 0.1 M. Polymerization studies of Bis Thiophen-carbazole fonctionnalized by fullerenes derivatives were also investigation to obtain polymers films with attractive photovoltaic properties.

[1]: *Handbook of Conducting Polymers*, ed. T. A. Skotheim,

[2] : P. Audebert ; S. Sadki ; F. Miomandre ; P. Hapiot ; K. Chane-Ching, *New J. Chem.* **2003**, 5, 798.

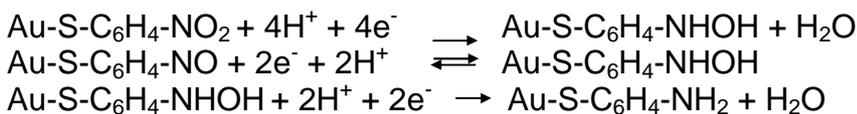
[3]: T. Rosenfeld, M. Ottolenghi , A. Y Meyer., *Mol. Photochem.*, 1973, 5, 39

Activated 4-nitrothiophenol modified Au electrodes as basis for amperometric biosensor applications

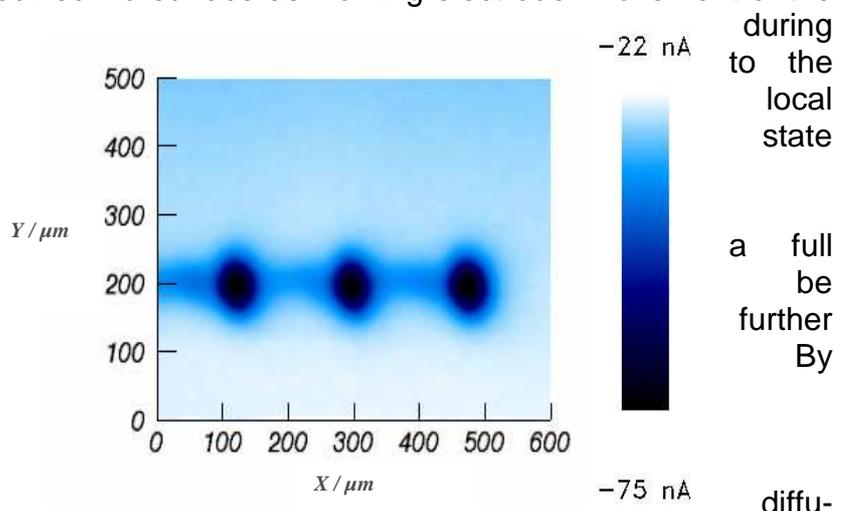
Stefanie Schwamborn, Leonard Stoica, Sebastian Neugebauer, Wolfgang Schuhmann

Analytische Chemie - Elektroanalytik & Sensorik, Ruhr Universität Bochum,
Universitätsstr. 150, D-44780 Bochum, Germany; email: stefanie.schwamborn@gmx.de

Nitroso/hydroxylamine redox couples have been shown to electrocatalytically mediate NADH oxidation as a basis for dehydrogenase-based amperometric biosensors [1]. Here, new aspects of the electrochemistry of 4-nitrothiophenol monolayers on Au electrode surfaces have been evaluated. Following chemisorption of 4-NTP on Au surfaces under formation of a dense self-assembled monolayer, the nitro groups can be selectively reduced to hydroxylamine intermediates avoiding the full reduction to aminothiophenol.



Localised reduction of the nitro groups (“writing”) can be realised using scanning electrochemical microscopy (SECM) in the direct mode, with the SECM tip used as counter electrode and the monolayer modified Au surface as working electrode. Movement of the SECM tip over the surface during application of reductive pulses working electrode generated modifications of the redox of the monolayer headgroups. Thereby a reduction to the hydroxylamine intermediate or reduction to amino groups can be achieved, which allows a modification of the Au surface. means of SECM in the feedback mode in the presence of hexacyanoferrat(III) as free- diffusing redox mediator the redox state of the surface bound species can be visualized (“reading”).



[1] a) Reda T., PhD thesis, 1999, TU-München. b) Mano N., Thienpont A., Kuhn A. *Electrochem. Comm.* (2001) 3, 585-589

Toward the engineering of nanostructured surfaces via self-assembly of peptide nucleic acids (PNAs)

Stefan Mohnani ^{†*}, Maurizio Prato [†], Davide Bonifazi ^{†‡}

[†] Dipartimento di Scienze Farmaceutiche, Università degli Studi di Trieste, Piazzale Europa 1,
34127 Trieste (Italy)

[‡] Laboratoire de Chimie Organique et des Matériaux Supramoléculaires (COMS), Facultés Universitaires
Notre-Dame de la Paix, 5000 Namur (Belgium)

* corresponding authors : gsmohnan@fundp.ac.be

The construction of grid-shaped self-assemblies on solid surfaces is the objective of this project. Programmed rigid molecular modules bearing unidirectional connectors, functionalized with peptide nucleic acids (PNA) will be used as the angular units for the surface assemblies. Complementary PNA oligomer strands will be used in linear units to connect the angular units together. Connection of the angular and linear units will occur via hydrogen bonding interactions between the nucleobases in the complementary PNA strands to form PNA duplexes. The magnitude of the domains of the self-assemblies will be in the range of 15-30 nm. Functionalization of the domains is envisaged to follow the construction of the nanostructure surface networks.

Electrochemical sensors based on hybrid inorganic-organic nanostructures coatings containing Prussian blue and conducting polymers

Stelian Lupu^{†*}, Cecilia Lete[‡], Mariana Marin[‡], Nicolae Totir[‡]
Laura Pigani[§], Fabio Terzi[§], Chiara Zanardi[§], Renato Seeber[§]

[†] Department of Analytical Chemistry and Instrumental Analysis, University Politehnica of Bucharest, Romania.

[‡] Laboratory of Electrochemistry, Institute of Physical Chemistry of the Romanian Academy, Bucharest, Romania

[§] Department of Chemistry, University of Modena and Reggio Emilia, Modena, Italy

* corresponding author : *Polizu Street 1-3, 011061 Bucuresti, Romania; e-mail: stelianl@yahoo.com

In the last two or even three decades there has been an increasing interest to the development of inorganic and organic modifiers for the electrode surface. In this frame, on the one side electrogenerated Prussian Blue (iron(III)hexacyanoferrate, PB) and PB derivatives and, on the other side, different conducting polymers, have been used as thin film electrode coatings. Both were shown to possess, to different extent, anti-fouling and electrocatalytic properties.

In this work, electrochemical preparation, characterisation and analytical applications of hybrid inorganic-organic films consisting of PB and of poly-[3,4-ethylenedioxythiophene] (PEDOT) have been considered. PB and PEDOT have been used for the preparation of hybrid films in two possible configurations, i.e. PB|PEDOT and PEDOT|PB. For both synthesis and characterisation of the coatings aqueous solutions have been used. The electrode modifications have been prepared electrochemically by a two-step method. In the case of the PB|PEDOT coating, first a PB layer has been electrodeposited onto a Pt electrode. In the second step, the electrochemical polymerisation of PEDOT film over the Pt|PB modified electrode has been carried out. In the case of the PEDOT|PB coating, an inner layer of organic conducting polymer has been first deposited onto Pt electrode and then the PB electrodeposition has been carried out by either potentiostatic or potentiodynamic method. The efficiency of deposition, the electrochemical behaviour and the stability to subsequent potential cycles have been evaluated by using electrochemical crystal quartz microbalance and cyclic voltammetry. These hybrid coatings exhibit electrocatalytic activity for the electrooxidation of ascorbic acid and dopamine. A linear dependence of the peak current of differential pulse voltammograms from 5×10^{-5} M to 5×10^{-3} M ascorbic acid concentration has been computed. A similar linear dependence from 1×10^{-4} M to 3×10^{-3} M dopamine concentration has also been obtained. These results demonstrate that hybrid inorganic-organic coatings containing PB and conducting polymers are suitable for electrochemical sensors development.

Acknowledgments: The financial support from the Romanian Ministry of Education and Research through grant CEEX 2006 – 1143/25.07.2006 is gratefully acknowledged.

Evaporated metal island films for special optical applications

Tanya Karakouz, Alexander Vaskevich, Israel Rubinstein

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

* e-mail: israel.rubinstein@weizmann.ac.il.

Evaporated noble metal (e.g. gold, silver) island films show a localized surface plasmon resonance, resulting in enhanced light scattering, the appearance of a characteristic absorption band, and enhancement of local electromagnetic fields. These properties have been used in surface-enhanced spectroscopies as well as in chemical and biological sensing. The latter application is based on the sensitivity of the surface plasmon band to changes in the effective refractive index of the contacting medium.

In the present work gold and silver island films (≤ 10 nm nominal thickness) were evaporated on glass substrates. The 3D shape of unannealed and annealed (at 200 °C and 550 °C) islands was analyzed using high-resolution SEM, cross-sectional TEM, and AFM imaging. The optical properties of the films were examined by transmission UV-vis spectroscopy.

Application of Au island films to gas sensing in the transmission localized surface plasmon resonance (T-LSPR) mode was demonstrated by spin-coating of polystyrene or polystyrene sulfonate onto 5 nm (nominal thickness) Au island films evaporated on silanized glass and annealed 20 h at 200 °C. Changes in the surface plasmon band (intensity, wavelength of maximum absorbance) observed upon exposure to certain vapors is attributed to vapor absorption and polymer swelling, effecting change in the refractive index of the islands' environment. The latter is manifested by the observation that the response to controlled amounts of vapors is distinctly different for vapors of good vs. poor solvents. The response is reversible and fast (~15 sec). Polymer-coated Au island films are therefore promising T-LSPR transducers for vapor recognition.

Formation of controlled roughness is essential in the preparation of substrates for surface-enhanced spectroscopies. Substrates comprising two-layered Au, Ag and Au-Ag island films in a sandwich configuration were prepared by evaporation of a 7.5 nm metal island film followed by deposition of an ultrathin organic layer and evaporation of a 2.5 nm metal island film. Preliminary results indicate that the Raman spectrum of 4-aminothiophenol obtained with Au-Au island sandwich films was an order-of-magnitude more intense than the spectrum obtained with a regular island film.

Structural analysis of mixed lipid bilayers on gold surface by means of PM IRRAS

Martina Nullmeier^{†*}, Izabella Zawisza[†], Gunther Wittstock[†]

[†] Carl von Ossietzky University of Oldenburg, Faculty of Mathematics and Science, Center of Interface Science (CIS), Department of Pure and Applied Chemistry and Institute of Chemistry and Biology of the Marine Environment, D-26111 Oldenburg, Germany.

*corresponding author : martina.nullmeier@uni-oldenburg.de.

The natural lipid membranes are liquid well ordered structures containing various lipids and proteins. It was found that the biological membranes contain rafts, which are composed of cholesterol and glycosphingolipids possessing large head groups composed of sugar and/or sialic acid residues. In these rafts in the hydrophobic hydrocarbon chain region the voids between associating glycosphingolipids are filled by cholesterol molecules which functions as a spacer. Little is known about the structural and conformational rearrangements taking place in the multicomponent lipid membranes. The unsymmetric three component lipid membranes containing DMPC, 30%-mol of cholesterol and 1 and 20%-mol of GM1 ganglioside were prepared on the gold surface. To produce the mixed lipid bilayer vertical Langmuir-Blodgett and horizontal touch Langmuir- Scheaffer methods were used. The produced lipid layer contains the ganglioside only in the outer layer and its content corresponds to quantities found in natural membranes.

Infrared reflection absorption spectroscopy (IRRAS) is widely used for studies of the structure of thin organized organic layers on surfaces reflecting the IR radiation, such as Au or Pt. The polarization modulation infrared reflection absorption spectroscopy (PM IRRAS) was used to characterize the structure of three component lipid bilayers on Au surface.

The IR spectra in the CH stretching mode region show that independently on the lipid content and surface pressure of transfer the hydrocarbon chains exist in liquid phase. Small intensity of the CH stretching modes point on long range order in the lipid layer. The average angle between the Ch stretching modes and the surface normal is equal to $70^\circ \pm 5^\circ$. Due to the presence of large numbers of gauche conformations the tilt of the hydrocarbon chains can not be quantitatively provided. The C=O stretching mode in the ester group of the DMPC phospholipid give rise the absorption which is deconvoluted into the bands centred at 1740 and 1724 cm^{-1} , pointing on different degrees of hydration of the ester group. The average tilt of the ester group is 64° when the lipid film contains 1%-mol GM1 and 70° for 20%mol GM1. The phosphate group of the phospholipid as well as amide groups in the ganglioside are hydrated. The structural picture of the three component lipid bilayer is provided.

Biological applications of transmission localized surface plasmon resonance (T-LSPR) spectroscopy

Tatyana A. Bendikov,[†] Aharon Rabinkov,[‡] Alexander Vaskevich,[†] Israel Rubinstein[†]

[†]Department of Materials & Interfaces and [‡]Biological Services Department,
Weizmann Institute of Science, Rehovot 76100, Israel

* e-mail: israel.rubinstein@weizmann.ac.il.

Discontinuous gold films (typically <10 nm nominal thickness) evaporated on transparent substrates show a localized surface plasmon (SP) extinction in the visible-to-NIR range, conveniently measured by transmission spectroscopy. The SP extinction band is highly sensitive to changes in the dielectric properties of the contacting medium, thus enabling to monitor the binding of molecular layers to the Au island film with submonolayer sensitivity. The method, termed transmission localized surface plasmon resonance (T-LSPR) spectroscopy, provides an effective scheme for label-free biological sensing using basic spectrophotometric equipment.

In the present work the applicability of T-LSPR spectroscopy (using Au island films) to monitoring specific antibody-antigen interactions is demonstrated. T-LSPR transducers were prepared by evaporation of 5 nm (nominal thickness) Au island films on silanized glass slides. Protein recognition interfaces were prepared by stepwise functionalization of the Au islands to carry carboxylate functionalities that covalently link to amino groups of the protein.

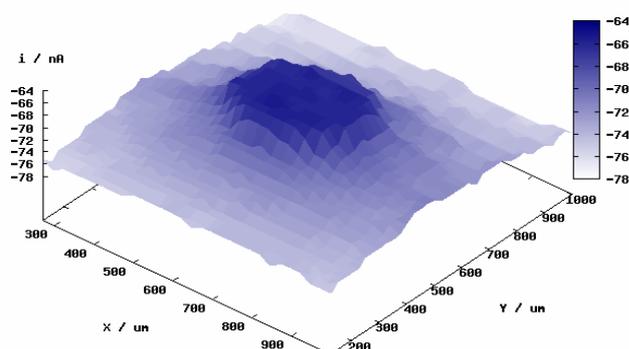
The protein-derivatized Au island films were used as a biological recognition surface for selective sensing of antigen binding, distinguishing specific and nonspecific interactions. Specific recognition of antigens was demonstrated using an array of four T-LSPR transducers. Further improvement of the system will allow application of the technique to fast, simultaneous determination of a number of proteins using detector arrays.

Application of the redox competition scanning electrochemical microscopy (RC-SECM) for the optimisation of biofuel cell cathodes using bilirubin oxidase/redoxpolymer spots

Yvonne Ackermann, Kathrin Eckhard, Dmitrii Guschin, Wolfgang Schuhmann

Analytische Chemie - Elektroanalytik & Sensorik; Ruhr-Universität Bochum
Universitätsstraße 150, 44780 Bochum

In recent years, the development of biofuel cells became more and more important. Enzymes can selectively catalyse the transformation of glucose and oxygen. An adequate immobilisation method guarantees easy miniaturisation of biofuel cells, since no longer a separator membrane between the electrode compartments is needed. A redox mediator, which is also immobilised on the electrode surface, is used for the electron transfer between electrode and enzyme. The redox potential and the electron transfer characteristics of the redox polymers can be fine-tuned by different coordinating ligands of redox-active Os-complexes. Design and optimisation of this multi-parameter system is rather complex. Therefore, efficient routines need to be developed in order to identify promising biofuel cell components.



Glucose oxidase is routinely used at the anode in biofuel cells. The interest of our research is focused on the cathode side because it is usually the limiting factor in biofuel cells. Billirubin oxidase is used together with polymer-bound Os-complexes as mediators to selectively catalyse the reduction of oxygen at the cathode. The concentrations of billirubin oxidase and the nature of the Os-modified anodic electrodeposition paints were varied to prepare a library of different cathode architectures. Spots were deposited on a glassy-carbon chip by means of a

piezoceramic microdispenser. Utilisation of this automated spot-preparing-system enabled the formation of reproducible spots of the same size and amount of substance. Afterwards, the activity of the enzyme/redoxpolymer spots were visualised (see graph) using scanning electrochemical microscopy (SECM) with the recently developed redox-competition mode [1,2].

[1] K. Eckhard, X. Chen, F. Turcu, W. Schuhmann, *PCCP* 8 (2006) 5359-5365. Redox-competition mode of scanning electrochemical microscopy (SECM) for visualisation of local catalytic activity

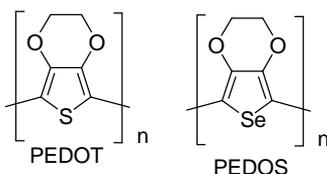
[2] K. Karnicka, K. Eckhard, D. Guschin, L. Stoica, P. Kulesza, W. Schuhmann, Visualisation of the local bio-electrocatalytic activity in biofuel cell cathodes by means of redox competition scanning electrochemical microscopy (RC-SECM) submitted to *Electrochem. Commun.*

Electrochemical and Spectroelectrochemical Study of Novel Polyselenophenes

Yair-Haim Wijsboom, Asit Patra, Sanjio S. Zade and Michael Bendikov*

Department of Organic Chemistry, The Weizmann Institute of Science, 76100 Rehovot, Israel

Despite of thousands of paper published on polythiophene and its derivative, very little is known on its close analog, polyselenophene and its derivatives. Thus no bulk highly conductive polyselenophene of any type has been reported. Polyselenophene should have similar or lower band gap than polythiophene and parent selenophene has better electron donating properties and lower oxidation potential compared to thiophene. Owing to its excellent electronic properties (electrical conductivity, electrochromic properties, relatively low band gap, etc.) and high stability, poly(3,4-ethylenedioxythiophene) (PEDOT) is the most studied and the most industrially important conjugated polymer. Recently we have developed a new, general and efficient synthetic strategy for the selenium analog of PEDOT, namely, poly(3,4-ethylenedioxyseleophene) (PEDOS). PEDOS is stable, completely insoluble in all common organic solvents, shows a π - π^* transition on-setting at around 900 nm and has a conductivity of about 10 S cm^{-1} (measured by the two probe method) after doping. We will present electrochemical and spectroelectrochemical study of PEDOS and some of its derivatives. The spectroelectrochemically measured band gap of PEDOS is 1.4 eV, which is in excellent agreement with our calculated (PBC-B3LYP/6-31G(d)) value.



Electrochemical Properties of thiol-based SAMs functionalized by Oligothiophenes ; structure and size -properties relationships

P. Lang* , S. Chebil , N. Battaglini

ITODYS ; CNRS – Université Paris7 ; 1 rue guy de la Brosse 75005 Paris

* lang@paris7.jussieu.fr

Conducting Polymers have given very interesting electronic and electrochemical systems. Immobilized on electrodes, oligothiophenes-based SAMs have notably given well-defined 2D systems^{1,2}.

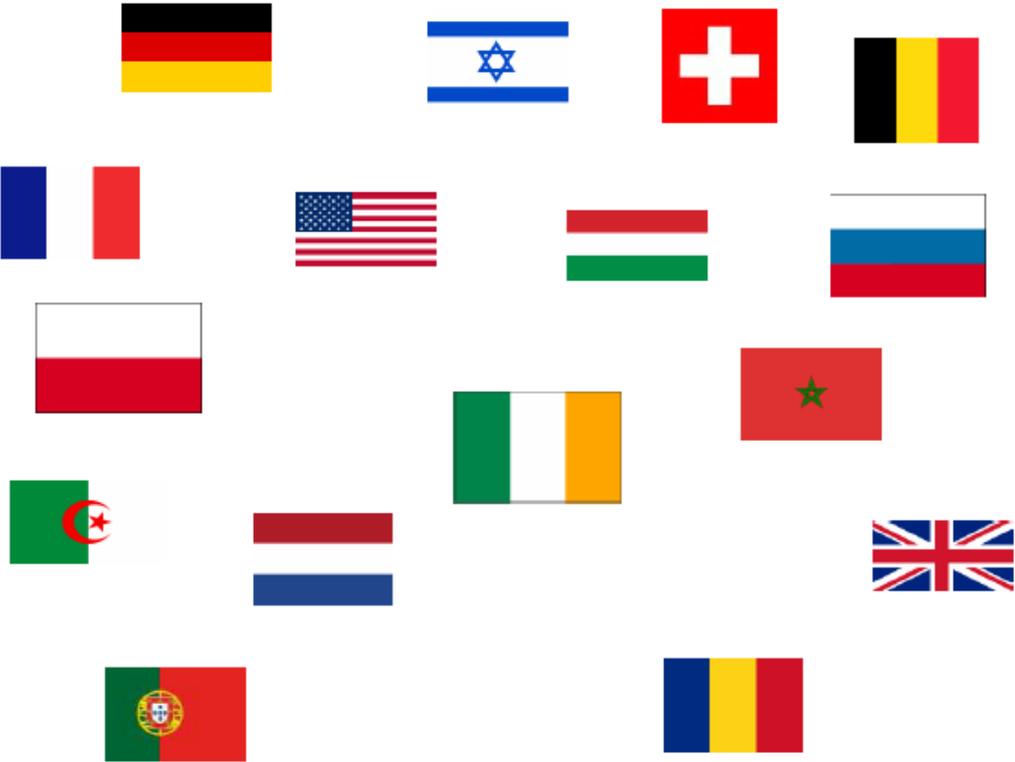
Our goal is to exhibit the relationship between on one hand the chemical structure and size of molecular grains in the SAM and on the other hand, redox and spectroscopic SAMs properties. By self-assembly, we envisage to build nanometer scale, ordered networks of electroactive organic monolayers by the replication of a spontaneously 2D structured metallic template such as Co/ Au single crystal³. The fundamental study of these objects will be made according to the knowledge necessary to their potential applications such as: i) electronics and electrochemistry on the scale of single or a few “semiconductor” molecules organized on nano-scaled networks, ii) biosensors, with in particular an application towards the sensitive detection of the hybridization of DNA strands.

In this preliminary study, we compare on macroscopic electrodes, both electrochemical and spectroscopic (IR) properties of thiol-based SAMs T₄-R-SH (T₄ is a quaterthiophene moiety), R is either an alkyl -(CH₂)_n or an oxoalkyl -CH₂-O- (CH₂)_n- spacer. With the alkyl spacer, monolayers are highly organized, crystal-like and give a voltammogram reversible from the first cycle and characteristic of large interactions between 4T moieties. On the other hand, the monolayer containing the oxoalkyl spacer is little organized and dense, permeable to water, solvent and ions with weak interactions between 4T moieties. The first anodic scan gives an irreversible chemical oxidation due to chemical coupling between the 4T units.

References :

- 1) M. Mottaghi, P. Lang, F. Rodriguez, A. Rumyantseva, A. Yassar, G. Horowitz, S. Lenfant, D. Tondelier, D. Vuillaume ; *Adv. Funct. Mat.* 17 (2006) 597,
- 2) C. Nogues, P. Lang, M. Rei Vilar, B. Desbat, T. Buffeteau, A. El-kassmi and F. Garnier ; *Colloids and Surfaces A* , 198 (2002) 577
- 3) V. Repain, G. Baudot, H. Ellmer and S. Rousset, *Europhysics Letters*, 58 (2002)730

Participants List



Abrantes Luisa
Ackermann Yvonne
Amato Claire
Amatore Christian
Arnould Christelle
Arurault Laurent
Asselberghs Inge
Auricchio Claudi
B.Nagy Janos
Bard Allen.J
Baudewijns Sébastien
Beckmann Michaela
Bendikov Tatyana
Bendikov Michael
Berger François
Bietlot Emerance
Bilewicz Renata
Bonifazi Davide
Buess-Herman Claudine
Burchardt Malte
Gallegari Vincent
Cecchet Francesca
Champagne Benoit
Chen Xingxing
Christophe Jennifer
Cornil Davide
Csoka Balazs
De Noose Vincent
Delhalle Joseph
Demellenne Laurent
Demoustier-Champagne
Sophie
Denayer Jessica
Detriche Simon
Devillers Sébastien
Eckard Kathrin
Einati Hila
Fonder Grégory
Fonseca Antonio
Franz Edith
Gebala Magdalena
Girault Hubet
Guenbour Abdellah
Guisset Charlotte
Golan Yuval
Gridelet Evelyne
Hapiot Philippe
Hojeij Mohamad
Hevesi Laszlo
Hihn Jean-Yves

Hussein Emad Mohamed
Idrissi Nabila
Issakova Tatiana
Janata Jiri
Janiak Sandra
Karakouz Tanya
Kauffman Jean-Michel
Keffous Aissa
Klink Stephan
Lafolet Frederic
Lai Stanley
Lallemand Fabrice
Lam Kevin
Lambert Magali
Lambin Philippe
Lang Philippe
Lebreux Frédéric
Lefèvre Isabelle
Leson Christian
Lete Cecilia
Lupu Stelian
Lyskawa Joël
Macanas Jorge
Maciewieska Monika
Maicka Elwira
Maljusch Artjom
Manjura Melanie
Martin Charles
Mekhalif Zineb
Minet Isabelle
Moens Dirk
Mohnani Stephan
Neugébauer Sébastien
Mullmeir Martina
Okunola Ayodele
Oulmi Kafia
Pähler Maike
Pêcheur Audrey
Plumier Fabian
Puschhof Andrea
Pust Sacha
Rubinstein Israel
Sadki Saïd
Seffer Jean-Francois
Schäfer Dominik
Schmuki Patrik
Schuhmann Wolfgang
Segut Olivier
Schwamborn Stefanie
Shacham-Diamand Yosi

Shkil Halyna
Simone Armani
Sinha Jatin Kumar
Souad El Hajaji
Steichen Marc
Stetzka Bettina
Stoica Leonard
Szucs Arpad
Tadjeddine Aberrahmene
Troiani Vincent
Van der Niet Janneke
Vaskevich Alexander
Vlachopoulos Nick
Wadhawan Jay
Weiss Paul
Wittstock Gunter
Yanson Alex
Ye Jian
Yolshina Lyudmila
Zawisza Isabella
Zoski Cynthia