# Program

# 5th Spring Meeting of the International Society of Electrochemistry

## Nanostructured Materials in Electrochemistry: Biosciences and Molecular Electronics Applications

1th May to 4th May, 2007
Dublin, Ireland

## Wednesday 2nd May – AM

### Synthesis and fundamental properties of nanostructured electroactive materials including nanolithography

9.10 -10.10 ***Richard M. Crooks***
Title Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles

10.10-10.40 Coffee Break

10.40-11.00 ***Jennifer Brennan***
Electrochemical Properties of a New Metallopolymer:Nanoparticle Nanocomposite Material

11.00-11.20 ***Xun Wei***
Morphological evolution of polycrystalline Platinum during electrochemical roughening

11.20-11.40 ***Ronan Baron***
Development of nanoelectrode arrays for sensing applications

11.40-12.00 ***Gabriela Kissling***
Electrochemical Properties of II-VI Quantum Dot Monolayers at Blocked Electrodes

## Wednesday 2nd May – PM

### Synthesis and fundamental properties of nanostructured electroactive materials including nanolithography

1.45-2.30 ***Ralph Nuzzo***
Mico Electrochemical Devices via Soft-Lithography: New Systems for Emergy and Bioanalytical Applications

2.30-2.50 ***Daniel Schwartz***
Use of crystalline proteins for templated electrodeposition

2.50-3.10 ***Jens-Peter Suchsland***
Particle Size and Substrate Effects in Electrocatalysis: Carbon and Titania Supported Gold Particles

3.10-3.30 ***Mathieu Etienne***
Nanostructured (organo)silica thin films on electrodes

3.30-4.00 Coffee Break

4.00-4.20 ***Daniel Buttry***
Synthesis and Characterization of Redox Active MnO2 Nanoparticles

4.20-4.40 ***Lukas Durrer***
Electrochemical Formation of Ni Catalyst Nanoparticles on Thin SiO2 Layers for SWNT Growth

4.40-5.00 ***Ralf Peipmann***
Electrocodeposition of Nickel-Alumina Nanocomposite Films under the Influence of Static Magnetic Fields

5.00-5.20 ***Kaido Tammeveski***
Kinetics of oxygen reduction on gold nanoparticle/multi-walled carbon nanotubes hybrid electrodes in acid solution

6.00-8.00 **Poster session**

## Thursday 3rd May – AM

### Biological applications

| | |
|---|---|
| 9.00-9.20 | ***Peter Weightman***<br>Reflection anisotropy spectroscopy of DNA adsorbed at the Au(110)/electrochemical interface. |
| 9.20-9.40 | ***Damien Arrigan***<br>Voltammetry of Pores, Particles and Proteins – Towards Nanobioelectroanalytical Systems |
| 9.40-10.00 | ***Alexander Volkov***<br>Nanoreactors in nature: Bioelectrochemical mechanisms |
| 10.00-10.20 | ***Renate Naumann***<br>A Spectroelectrochemical Approach to Complex Membrane Proteins |
| 10.20-10.45 | Coffee Break |
| 10.45-11.30 | ***Hubert Girault***<br>Nanoparticles on surfaces for proteomic analysis |
| 11.30-11.50 | ***Emmet O'Reilly***<br>Electrochemiluminescent Metallopolymers for Detection of Biological Analytes |
| 11.50-12.10 | ***Sebastian Neugebauer***<br>DNA Sensors in Selectively Modified Nanoporous Electrode Structures |
| 12.10-12.30 | ***Nicolas Plumeré***<br>Synthesis, characterization and electrochemistry of redox-modified silica particles on platinum electrode surfaces |

## Thursday 3rd May – PM

### Biological applications

| | |
|---|---|
| 2.00-2.45 | ***Philip Bartlett***<br>Engineering SERS Substrates for Bioelectrochemical Studies |
| 2.45-3.05 | ***Judith Rishpon***<br>Electrochemical Detection of Biological Reactions Using a Novel Nano-Bio-Chip Array |
| 3.05-3.25 | ***Gerald Kada***<br>Nano-electrochemistry on the AFM-Tip applied to live cells |
| 3.25-3.45 | ***Chin-Pei Chen***<br>Label-Free DNA Sensing using GAN nanowires Naonosensors |
| 3.45-5.30 | **Poster session** |

## Friday 4th May – AM

### Biological applications

| | |
|---|---|
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| 9.20-9.40 | ***Christine Mousty***<br>Layered Double Hydroxides-Enzyme nanohybrid materials applied to biosensor development |

## Friday 4th May – AM *continued*

### Biological applications

| | |
|---|---|
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| 10.00-10.20 | ***Emmanuel Iwuoha***<br>Nanobiosensor for amperometric capture of the metabolic profile of antiretroviral drugs |
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| 11.00-11.20 | ***Emil Palecek***<br>Self-Assembled Monolayers at Electrodes in DNA and Protein Analysis |
| 11.20-11.40 | ***Alexander Vaskevich***<br>Biological and Chemical Sensing Using Transmission Localized Surface Plasmon Resonance (T-LSPR) Spectroscopy |
| 11.40-12.00 | ***Lihua Bi***<br>Simple Preparation Method of Multilayer Films Containing Pd Nanoparticles |
| 12.00-12.20 | ***T. F. Otero***<br>Electrochemical relaxation loop, conformational energy and conformational memory. (Is brain memory stored by polymeric conformations?) |

## Friday 4th May – PM

### Molecular electronics applications

| | |
|---|---|
| 1.45-2.30 | ***Ulstrup Jens***<br>Single-molecule “Transistors” from Au-nanoparticles to Proteins and DNA in Electrochemical Environment |
| 2.30-2.50 | ***Harm van Zalinge***<br>The Influence of the Electrode Material on the Single Molecule Conductance |
| 2.50-3.10 | ***Tohru Kawamoto***<br>Multi-color Electrochromism of Nanoparticles of Prussian blue and Its Analogues |
| 3.10-3.30 | ***Claire Amato***<br>Functionalized Gold Surfaces of Polyfluorinated Dithiols as New Platform for Electronic Devices |
| 3.30-4.00 | Coffee Break |
| 4.00-4.20 | ***Edmund Leary***<br>Single molecule electronic behaviour of á, á’–bis(6–mercaptohexyl)oli gothiophenes and related compounds. |
| 4.20-4.40 | ***Nick Vlachopoulos***<br>Electrochemical aspects of nanostructure display technology based on titanium dioxide-attached viologen chromophores |
| 4.40-5.00 | ***Kenneth Ozoemena***<br>Novel Electroactivities of Nanostructured Metallophthalocyanine Single-Walled Carbon Nanotube Arrays at Gold Surfaces |

Book of Abstracts of the

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# Invited Lectures

# Title Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles

Heechang Ye and Richard M. Crooks*
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Pt and Pd monometallic and Pt-Pd bimetallic (alloy) nanoparticles containing up to an average of 180 atoms were prepared within sixth-generation, hydroxyl-terminated, poly(amidoamine) dendrimers. These dendrimer-encapsulated nanoparticles (DENs) are prepared using a two-step synthesis. First, the dendrimers are mixed with a solution containing a predetermined ratio of $PtCl_4^{2-}$ and $PdCl_4^{2-}$. For example, the synthesis of 50:50 Pd:Pt alloy DENs is carried out using an equimolar mixture of the Pt and Pd ion complexes (each present in 90-fold excess with respect to the dendrimer concentration). This first step results in complexation of the metal ions to tertiary amine groups within the dendrimer. Next, a reducing agent, such as $BH_4^-$, is added to the solution, which converts the metal ions to individual nanoparticles that remain encapsulated within the dendrimer. Transmission electron microscopy, electron diffraction, energy dispersive X-ray spectroscopy (EDS), UV-vis spectroscopy, high-energy X-ray diffraction, and EXAFS measurements confirme that the size and composition of these materials can be precisely controlled using this synthetic approach. For example, EDS indicated that nanoparticle composition was determined by the percentage of each element used during the first step of the synthesis. However, some interesting structural anomalies were observed for Pt-only nanoparticles. Following characterization, the DENs could be immobilized on glassy carbon (GC) electrodes using a simple electrochemical procedure. Experiments designed to identify the location of the nanoparticles following immobilization confirmed that they remained encapsulated within the dendrimers. The total surface area of the Pt-only DENs was measured by hydrogen adsorption and found to be 0.22 $cm^2$, which can be compared to a calculated surface area of 0.16 $cm^2$ determined by assuming monolayer coverage of spherical DENs consisting of 180 atoms. Cyclic voltammetry and quantitative rotating disk voltammetry were used to measure the electrocatalytic properties of mono- and bimetallic DENs for the oxygen reduction reaction (ORR). Particular compositions of the bimetallic nanoparticles exhibited a rate enhancement of up to a factor of 2.5 compared to monometallic Pt. However, the most important result of this project is the demonstration that electrocatalysts containing just 180 atoms and having uniform compositions can be synthesized and characterized ex situ and then subsequently be immobilized on an electrode surface. This provides a direct means to correlate the structure of the nanoparticles to their electrocatalytic function. This approach can be contrasted wtih in-situ synthetic approaches, which usually lead to polydisperse catalysts that are difficult to fully characterize. The DEN synthesis can also be used to prepare core/shell nanoparticles, and a discussion of how density functional theory (DFT) can be used to predict the electrocatalytic properties of such materials will be presented.

# Micro Electrochemical Devices via Soft-Lithography: New Systems for Energy and Bioanalytical Applications

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This talk will describe advances in methods of materials processing and patterning that appear to hold significant potential for enabling applications of microelectrochemical systems in diverse areas of technology. This talk will describe new forms of soft-lithography and the properties of specific exemplary demonstrations of microelectrochemical systems fabricated using them. Of particular interest in this regard are rapidly advancing capabilities of fabrication protocols based on soft-embossing—methods that are uniquely suited to the construction of complex multi component systems based on microfluidic architectures, advanced integrated sub-wavelength optics, MEMS, amongst other forms of functional integrated devices. I will describe recent work in our laboratory that has led to the development of several interesting microelectrochemical platforms—notably an embedded microfluidic cell architecture and optically integrated semiconductor devices with novel form factors. The former system is one that has remarkable properties as a form of chemical actuator and examples of its use in systems spanning from bioanalytical sensing to fuel cells will be highlighted. The second device class holds broad utility for sensing and energy conversion—leading applications that will inform discussions of emerging prospects for functional macroscale systems whose properties follow from the nature of the high performance microelectrochemical components they embed.

# Engineering SERS Substrates for Bioelectrochemical Studies

Philip N. Bartlett*,
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Templated electrochemical deposition through close packed monolayers of unform polystyrene colloidal particles followed by dissolution of the template produces structured thin films containing an array of interconnected spherical segement voids. The diameters and organisation of these voids replicate the diameter and packing of the colloidal particles used to form the template and the thickness of the film is controlled by the charge passed to deposit the film. It is thus possible to simply and predictably control the geometry of the film. These structured metal films have interesting magnetic [1], superconducting [2] and optical properties [3] that are determined by their precise geometry.

Using templates with diameters between 450 and 1200 nm we are able to produce surfaces that show significant enhancement in surface enhanced Raman spectroscopy (SERS). We have investigated the origins of this surface enhancement by varying the film thickness, template sphere diameter and looking at the angular dependence. We find that the intensity of the SER spectra varies with all of these factors indicating that the precise geometry of the structured surface and the excitation of surface plasmons is important. In contrast to electrochemically roughened surfaces the intensity of the SERS spectra on the structured surface is reproducible from place to place across the surface and from sample to sample. This is a significant potential advantage. The structured surfaces are also robust and stable under laboratory conditions and ideally suited as electrodes for electrochemical SERS experiments.

Visible excitation laser sources commonly used in SERS experiments can cause photochemical reactions on the surface as well as fluorescence from the adsorbed molecules, such problems are prevalent in the study of biomolecules. A way to circumvent this possibility is the use of Near Infra-Red (NIR) laser sources. This demands appropriate design of substrates for NIR-SERS in order to obtain the maximum enhancement. Results will be presented for a series of adsorbed analytes and biologically relevant molecules.

References

[1] P. N. Bartlett, M. A. Ghanem, I. S. El Hallag, P. de Groot, A. Zhukov, *J. Mater. Chem.*, **13**, 2003, 2596.
[2] A. A. Zhukov, E. T. Filby, M. A. Ghanem, P. N. Bartlett and P. A. J. de Groot, *Physica C*, **404**, 2004, 455.
[3] P. N. Bartlett, J. J. Baumberg, S. Coyle and M. Abdelsalem, *Faraday Discuss.*, **125**, 2004, 117.
[4] S. Mahajan, M. Abdelsalam, Y. Suguwara, S. Cintra, A. Russell, J. Baumberg and P. Bartlett, *Phys. Chem. Chem. Phys.*, **9**, 2007, 104.

# Nanoparticles on surfaces for proteomic analysis

J-P. Abid[1], J-M. Busnel[1], J. Gamby[1], J. Ji[2] , B.H.Liu[2] *, Y. Liu[2] , N. Lion[1] , Y. Xue[2] , P. Yang[2] , M. Zhang[1], H. H. Girault[1] *,

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Proteomics involves the analysis of the protein content of a biological sample at a given time. Many techniques are currently used to address this topic. In this lecture, we shall discuss different analytical techniques associated to the use of nanoparticles.

**In chip protein digestion** : Laser photoablated microchannels are coated with gold nanoparticles and poly(diallyldimethylammonium chloride). This surface is then used to immobilise trypsin The maximum proteolytic rate of the adsorbed trypsin was 400 mM/(min·$\mu$g), much faster than that in bulk solution due to the biocompatible microenvironment provided by the gold nanoparticles. The controlled amount of adsorbed trypsin was studied on the basis of the Langmuir isotherm, and the fitted $\Gamma_{max}$ and $K$ values were estimated to be $1.2\times10^{-7}$ mol·m$^{-2}$ and $4.1\times10^{5}$ M$^{-1}$, respectively. Trace amounts of standard protein samples down to 16 fmol were confidently digested using the enzymatic microreactor and resulting tryptic products were identified by MALDI-TOF MS/MS.

**In chip protein adsorption** : We present the detection of ultralow concentrations of biomolecules in a device made from a polycarbonate membrane containing a network of gold nanowires and using contactless impedance spectroscopy. The sensor comprises a thin dielectric layer with two parallel band electrodes on the one side, and a microchannel containing gold nanowires onto which the adsorption of antibodies occurs. Upon applying a high frequency AC voltage between the two electrodes, the adsorption process occurring at the surface of the gold nanowires can be followed through contactless impedance measurements. The configuration allows the real-time detection of biomolecules with a bulk concentration in the picomolar range.

**SECM of silver stained proteins on PVDF membranes:** Silver staining is a classical method to visualize proteins in gels after electrophoresis or on PVDF membranes after Western blot. In fact, silver staining consists in the reduction of silver salts yielding silver nanoparticles. We show here that SECM is a very sensitive electrochemical technique to quantitatively detect these nanoparticles and can be used to map proteins after blotting. We also show how SECM can be used to record fingerprints.

# Single-molecule “Transistors” from Au-nanoparticles to Proteins and DNA in Electrochemical Environment

*J. Ulstrup*
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Scanning tunnelling microscopy (STM) to molecular resolution in *aqueous solution* under substrate and tip double potential control (*in situ* STM) is established and has recently been extended in our group to ionic liquid media. *In situ* STM extends beyond imaging, and offers *two* kinds of tunnelling “spectroscopy”, the tunnelling current/*bias* voltage relation at constant electrochemical *overpotential*, and the tunnelling current/*overpotential* relation at constant *bias voltage*. These are equivalent to the current/bias and current/gate voltage relations of molecular transistors. In contrast to reported cases of single-molecule transistors, *in situ* STM-based molecular transistor function operates at *room temperature* in *condensed matter* environment. The accessibility of a chemical *redox centre* in the molecule is crucial in this respect.

*In situ* STM-tunnelling spectroscopy with “on-off” ratios up to two orders of magnitude is established in our group, with transition metal complexes and a redox metalloprotein (*Pseudomonas aeruginosa* azurin) as prime targets. New results apply to Coulomb blockade effects in Au-nanoparticles (1.6 nm) and to redox-marked oligonucleotides. These quite different systems display molecular electronic amplification features that, however, differ in details of the physical mechanisms. Some perspectives of this will be noted.

# Oral Presentations

# Functionalized Gold Surfaces of Polyfluorinated Dithiols as New Platform for Electronic Devices

Claire Amato, Patrick Calas, Joseph Delhalle, Zineb Mekhalif
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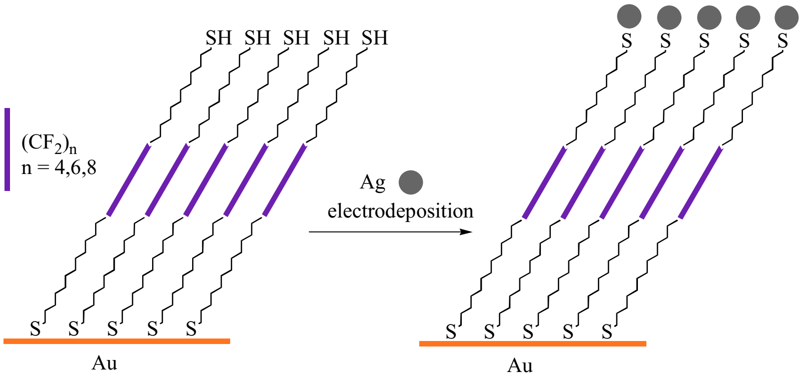
To overcome the technological and physical limits of microelectronic devices, metal/molecule/metal (MMM) junctions are currently envisioned[1]. According to the electronic properties of organic molecules used, these new molecular electronic components have found applications as molecular rectifier, molecular 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 for the target substrate. To be involved in MMM junctions, only one functional group must bond to the substrate to allow the further metallization of the leaving terminal group disposed away from the surface.



Herein we presented the self-assembly of polyfluorinated dithiol molecules onto gold surface and their metallization by silver atoms. Syntheses of difunctional polyfluoroalkane molecules are firstly reported. Then SAMs formation is studied as a function of time and solvent incubation by Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), Polarisation Modulation-Infra Red Reflection (PM-IRRAS), X-ray Photoelectron Spectroscopy (XPS) and contact angle measurements. Finally Ag electro-deposition on SAMs that present only one thiol bond to the gold substrate was realized by Cyclic Voltammetry (CV) and demonstrated by Electronic Scanning Microscopy (ESM).

1 D. Vuillaume, S. Lenfant, *Microelectronic Engineering*, 70, **2003**, 539-550.

# Voltammetry of Pores, Particles and Proteins – Towards Nanobioelectroanalytical Systems

Damien W. M. Arrigan*, Alfonso Berduque, Gregoire Herzog, Yvonne Lanyon
*Tyndall National Institute, Lee Maltings, University College, Cork, Ireland*
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Electrochemistry and nanotechnology offer many means for the solving of biological measurement problems such as trace protein detection. The simplicity of electrochemical methods combined with their possibilities for miniaturisation and portability makes them attractive as simple tools for solving many types of molecular measurement problems. We aim to develop biologically-inspired molecular measurement systems, which combine micro- and nanotechnology tools with electrochemical processes. The methods and technologies we study are important in the development of new diagnostic devices, pharma/biopharma analysis, environmental monitoring and industrial process control. In all of these areas, the need for chemical and biochemical information is paramount and simple tools (methods, devices, microsystems) for Information Harvesting are needed. In this presentation we will highlight some examples of our recent achievements in these areas including (i) the miniaturisation of electrochemical interfaces within micromachined silicon and nanomachined silicon nitride pores (and nanochannels) in order to enhance mass transport (diffusion) and hence electrochemical sensitivity, (ii) the study of the electrochemical behaviour of biomolecules at electrified liquid-liquid interfaces, and (iii) the study of the behaviour of dendrimers, important biomimetic macromolecular nanoparticles, at liquid-liquid interfaces. These examples encompass our interests in exploring nanoelectrochemical processes of bioanalytical importance as a basis for the development of bio-inspired molecular measurement systems for various applications. Specific examples from recent investigations will be presented.

# Development of nanoelectrode arrays for sensing applications

Ronan Baron, Biljana Šljuki , Xuan Dai, Gregory G. Wildgoose, Richard G. Compton*,

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Several strategies have been investigated for the practical realization of random nanoelectrode arrays and their use for sensing applications. In our approach, different kind of metal nanoparticles were synthesized on glassy carbon microspheres and the resulting hybrid material was used for the design of various nanoelectrode arrays.

(I) The combinatorial screening of different metallic nanoparticles as electrocatalysts was investigated and efficiently applied for the detection of hydrazine and bromide ions [1,2]. In a first step, glassy carbon microspheres decorated with metallic nanoparticles (Au, Pd and Ag) were abrasively attached on the surface of a basal plane pyrrolytic electrode giving a ‘multi-metal’ nanoarray. In a second step, electrodes modified with only one type of metallic nanoparticles allowed the identification of the catalytic material.

(II) The immobilization of glassy carbon microspheres decorated with metal nanoparticles was also investigated with the construction of metallic nanoparticles/glassy carbon microspheres/carbon nanotube composite thin film on glassy electrode surfaces and such architecture was used for multi-analyte sensing [3,4].

(III) Carbon-epoxy composite electrodes loaded with the metal nanoparticles were designed for a practical use. The carbon-epoxy composite nanoarray electrodes was found to have excellent characteristics as for the sensing of hydrazine and bromide ions [1,2].

[1] B. Šljuki , R. Baron, C. Salter, A. Crossley, R.G. Compton, (2007). Submitted.

[2] R. Baron, B. Šljuki , C. Salter, A. Crossley, R.G. Compton, (2007). Submitted.

[4] X. Dai, G.G. Wildgoose, C. Salter, A. Crossley, R.G. Compton, Anal. Chem., 78 (2006) 6102.

[5] X. Dai, G.G. Wildgoose, R.G. Compton, Analyst, 131 (2006) 1241.

# Simple Preparation Method of Multilayer Films Containing Pd Nanoparticles

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The design and construction of nanoparticles have been the focus of recent materials research interest because of their unique electronic, catalytic, and optical properties.[1] Noble metal nanoparticles are of fundamental interest and technological importance because of their applications as catalysts.[2] In the most interesting and practically promising field, such as sensors and photo- or bio-electrochemical devices, the nanoparticles are utilized in the form of thin films deposited on suitable substrates.[3] The layer-by-layer (LBL) assembly method initially developed for pairs of oppositely charged polyelectrolytes has been recently applied to the preparation of the three-dimensional superstructure array of nanoparticles.[4] It allows for the deposition of homogeneous, robust films with accurately controlled layer thickness and interlayer separation. However, most of the nanoparticles must be pre-synthesized through reduction of a metal salt by reducing agents in solution. In this study, a direct synthetic method of three-dimensional nanoparticle multilayer films by a LBL technique on a GCE surface is described. First, on the 4-aminobenzoic acid (4-ABA)-functionalized GCE, the $Os^{2+}$ functionalised pyrrole monomer, osmium-bis-N, N´-(2,2´-bipyridyl)-N-(pyridine-4-yl-methyl-(8-pyrrole-1-yl-octyl)-amine)chloride (BPPA-Os)[5] and $[Cs_2Na(H_2O)_{10}Pd_3(a\text{-}SbW_9O_{33})_2]^{9-}$ $(Sb_2W_{18}Pd_3)$[6] are alternately assembled by electrostatic interaction. Second, $Pd^{2+}$ is electrochemically reduced to yield zero valent Pd particles. Thus, the nanoparticles can be uniformly distributed in the multilayer films and the amount of nanoparticles on GCE can be controlled conveniently.

## References:

1. Gur, I.; Fromer, N. A.; Geier, M. L.; Alivisatos, A. P. *Science,* 2005, 310, 462-465.
2. Hughes, M. D.; Xu, Y. J.; Jenkins, P.; McMorn, P.; Landon, P.; Enache, D. I.; Carley, A. F.; Attard, G. A.; hutchings, G. J.; King, F.; Stitt, E. H.; Johnston, P.; Griffin, K.; Kiely, C. J. *Nature,* 2005, 437, 1132-1135.
3. Sun, X. P.; Du, Y.; Zhang, L. X.; Dong, S. J.; Wang, E. K. Anal. Chem. 2006, 78, 6674-6677.
4. Sun, X. P.; Du, Y.; Dong, S. J.; Wang, E. K. 2005, 77, 8166-8169.
5. Foster, K.; Allen, A.; McCormac T. J. Electroanal. Chem. 2004, 573, 203-214.
6. Bi, L. –H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R. J. Inorg. Chem. 2004, 43, 3915-3920.

# Electrochemical Properties of a New Metallopolymer:Nanoparticle Nanocomposite Material.

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Nano-sized and nanostructured materials demonstrate radically different spectroscopic, electronic and catalytic properties to bulk materials.[1] These novel properties have led to current and future applications in areas as diverse as molecular electronics, drug and gene delivery, medical diagnostics, chemosensing, solar energy harvesting and personal care products, to name but a few examples.[1,2] Our interest in nanomaterials focuses on the development of new high-performance platforms for biomedical diagnostics. One successful outcome has been the use of thin films of a metallopolymer, $[Ru(bpy)_2(PVP)_{10}]^{2+}$, where bpy is 2,2-dipyridyl and PVP is poly(4-vinylpyridine), to detect DNA using combined light and current detection via an electrochemiluminescent reaction (ECL) between DNA and the metallopolymer.[3] Our goal is to modulate the charge transport, spectroscopic and overall ECL efficiency of the metallopolymer by creating a nanocomposite material where nano-sized gold particles are incorporated into the thin films. To achieve this, 1.6 nm diameter gold nanoparticles capped with a mixed monolayer of hexanethiol and 11-mercaptoundecanoic acid were prepared and characterized.[4,5] These materials are in the quantum size region and electrochemical investigation reveals the presence of up to 13 well-defined quantized charge states. However, the UV-vis spectrum of the particles does not show the well-defined surface plasmon band displayed by larger particles. These nanoparticles were incorporated into the metallopolymer and the electrochemical properties of thin films of the polymer were studied, demonstrating that the nanocomposite material displays radically different charge transport properties to the metallopolymer alone. The electronic conductivity and spectroscopic behaviour of the nanocomposite is under investigation and will be described in detail.

References:
1. Katz, E.; Willner, I *Angew. Chem. Int. Ed.* 2004, *43*, 6042.
2. Daniel, M. C.; Astruc, D. *Chem Rev.* 2004, *104*, 293.
3. Dennany, L.; Forster, R. J.; Rusling, J. F. *J. Am. Chem. Soc.* 2003, *125*, 5213.
4. Song, Y.; Murray, R. M. *J. Am. Chem. Soc.* 2002, *124*, 7096.
5. Brennan, J.L.; Branham, M.R.; Hicks, J.F.; Osisek, A.; Donkers, R.L; Georganopoulou D.G.; Murray, R.W. *Analytical Chemistry* 2004, *76*, 5611-5619.

# Synthesis and Characterization of Redox Active $MnO_2$ Nanoparticles

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In this contribution, we will describe the synthesis and characterization of "bare" nanoparticles of $MnO_2$ as well as $MnO_2$ nanoparticles that are encapsulated with poly(ethylenedioxythiophene) (PEDOT). The synthesis of $MnO_2$ NPs is based on a protocol initially described by Suib and coworkers.[1] This produces colloidal solutions of $MnO_2$ NPs in the 3-5 nm diameter size range. Figure 1 shows a high resolution TEM of $MnO_2$ NPs obtained using such a procedure. The image reveals lattice fringes that are characteristic of the layered birnessite structure of this material. AFM also is used as a routine tool for size characterization. The presentation will describe several AFM images of $MnO_2$ NPs immobilized by evaporation on a mica substrate. These $MnO_2$ NPs can be assembled into thin film structures on electrodes using a layer-by-layer method with poly(diallyldimethylamine) (PDDA) (chloride salt) as an electrostatic binding agent. Figure 2 shows the results of cyclic voltammetric experiments for thin films containing 1-5 layers of $MnO_2$ NPs bound with alternating layers of PDDA. The electrochemical characterization of these electroactive NPs will be described. We also will describe the synthesis and characterization of PEDOT encapsulated $MnO_2$ NPs prepared by reduction of $MnO_4^-$ using EDOT, the PEDOT monomeric precursor. HRTEM and scanning tunneling spectroscopy are used to characterize the PEDOT-encapsulated $MnO_2$ NPs.

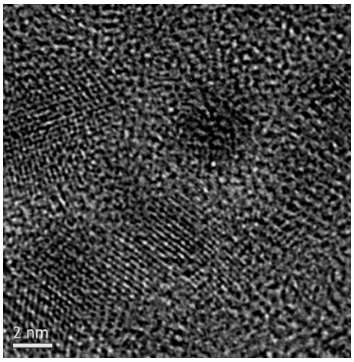

*Figure 1*

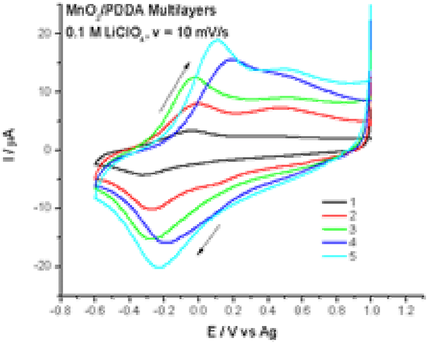

*Figure 2*

(1) Brock, S. L.; Sanabria, M.; Suib, S. L.; Urban, V.; Thiyagarajan, P.; Potter, D. I. *J. Phys. Chem. B* **1999**, *103*, 7416 - 7428.

# ELECTROCHEMICAL FORMATION OF Ni CATALYST NANOPARTICLES ON THIN $SiO_2$ LAYERS FOR SWNT GROWTH

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We investigated the chronoamperometric and potentiometric formation of Ni nanoparticles on $Si/SiO_2$ surfaces. These particles were used as catalyst for the growth of individual single-walled carbon nanotubes (SWNTs) by low pressure chemical vapor deposition (LPCVD) of $CH_4$ as carbon source.

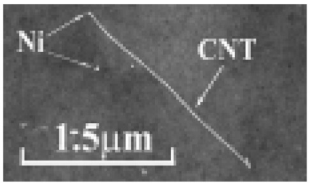

Fig. 1: AFM image of a CNT grown by LPCVD on a Ni particle, which was formed on a $Si/SiO_2$ electrode by a 8.2mA/cm$^2$ current pulse of 50µs from a 10mM $H_3BO_3$ + 10mM $NiSO_4$ electrolyte solution. z-range: 5nm

SWNTs have shown remarkable electrical and electromechanical properties, which makes them interesting to use as sensing elements in chemical, biochemical and electromechanical sensors. For batch production of CNT-based devices, fundamentals in the CNT growth, in particular the control of the CNT chirality, density and growth direction still have to be investigated. Several studies have shown that in the chemical vapor deposition (CVD) process, the catalyst size and the catalyst surface densities influence CNT diameter and CNT surface densities respectively. There exist already many routs of catalyst formation. Since Ni catalyze the $H_2$ evolution, chronopotentiometric and chronoamperometric Ni seed crystal formation would have the advantage of a fast, low cost, size and density controlled catalyst formation for the CVD growth of CNTs [1]. However, because electrochemical deposition requires conductive surfaces, whereas CNT growth is mostly performed on dielectrical ones, it has only been possible to grow multi-walled CNTs on electrochemically formed Ni particles with diameter larger than 50nm on Cr surfaces [2]. We investigated the chronoamperometric and chronopotentiomeric formation of Ni nanoparticles from a 10 mM $H_3BO_3$ + 10mM $NiSO_4$ electrolyte solution on thermally grown $SiO_2$ surfaces with thicknesses between 20 and 28nm, by taking advantage of the electron tunneling trough the oxide layer. The particle densities and diameters were analyzed by AFM imaging. It was observed, that besides deposition current densities, pulse times and pulse potentials, the particle sizes and surface densities strongly depend on the leakage current of the $SiO_2$ layer. We were able to form Ni nanoparticles with mean sizes between 0.7 and 3 nm. As shown in Fig. 1, this enabled us for the first time to grow SWNTs with diameters between 0.5 and 2 nm on electrochemically formed catalyst nanoparticles.

[1] MP. Zach, RM. Penner, Advanced Materials 12 (2000) 878
[2]Y. Tu, ZP. Huang, DZ. Wang, JG. Wen, ZF. Ren, Applied Physics Letters 80 (2002) 4018

# Nanostructured (organo)silica thin films on electrodes

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Electrochemistry of sol-gel-derived silica-based materials has gained great popularity in recent years [1]. Silica and organosilica films with tailor-made properties can be easily prepared on various electrode surfaces and advantageously exploited for several applications, especially in electroanalysis [2]. Recently, it has been shown that structuration of these films at the mesoporous scale offer great promise to extend their scope of applications in various fields of electrochemistry [3]. Nanostructured silica films can be deposited onto the surface of solid support by the so-called "Evaporation-Induced Self-Assembly" (EISA) technique, which is likely to form thin films with various ordered mesostructures such as p6m (2D hexagonal), P6$_3$/mmc (3D hexagonal) and Pm3n (cubic) [4]. Using cetyltrimethylammonium bromide as the template, it was possible to prepare mesoporous silica thin films with various structures and thicknesses on solid electrode surfaces. Their permeation properties were characterized by cyclic voltammetry and wall-jet electrochemistry using electrochemical probes displaying various charges and sizes (I$^-$, Fe(CN)$_6^{3-}$, Ru(bpy)$_3^{2+}$, FcMeOH) [5]. The organization of the porous network constituting the silica film and its stability in aqueous medium were found to have a profound effect on its permeability properties and the following sequence was observed by cyclic voltammetry: Pm3n > P6$_3$/mmc ≈ Im3m > P6m. The electrochemical responses were also dramatically influenced by the charge and the size of the molecular. Positively-charged species were likely to accumulate into the film while negatively-charged species can be totally or partially excluded, leading to preconcentration and permselective behaviors. Quantitative permeability measurements for the molecular probes in thin films with cubic mesostructure were made using the wall-jet electrochemistry technique. Thiol-functionalized mesoporous silica films were also prepared and their suitability to be applied for preconcentration electroanalysis has been studied using Hg$^{2+}$ and Ag$^+$ as model analytes [6, 7]. The performance of the modified electrodes was found to be dramatically influenced by the composition of the sol used to prepare the thin films, and especially its surfactant content. The best results were obtained with materials displaying highly open mesostructures with readily accessible thiol groups in the mesopore channels.

[1] A. Walcarius, D. Mandler, J. Cox, M.M. Collinson, O. Lev, J. Mater. Chem., 2005, 15, 3663.
[2] A. Walcarius, Chem. Mater., 2001, 13, 3351 & Electroanalysis, 2001, 13, 701.
[3] A. Walcarius, C.R. Chim., 2005, 8, 693.
[4] D. Grosso, F. Cagnol, G.J.A.A. Soler-Illia, E.L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, C. Sanchez, Adv. Funct. Mater., 2004, 14, 309.
[5] M. Etienne, A. Quach, D. Grosso, L. Nicole, C. Sanchez, A. Walcarius, Chem. Mater., in press.
[6] M. Etienne, A. Walcarius, Electrochem. Commun., 2005, 7, 1449.
[7] M. Etienne, J. Cortot, A. Walcarius, Electroanalysis, in press.

# Nanobiosensor for amperometric capture of the metabolic profile of antiretroviral drugs

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Antiretroviral drugs work by maintaining a plasma level at the human immunodeficiency virus (HIV) replication site sufficient enough to inhibit viral mutation and viral resistance, and suppress viral load of patients. This requires that dosing level of the drugs be such that should express the expected anti-HIV effect with minimal toxicity. Biosensors can be used to provide real time information on the metabolic profile of the drug necessary for modulating therapy to the patient's benefit. In this study, antiretroviral drugs nanobiosensor system was developed with human cytochrome P450 3A4 (CYP3A4) and layer-by-layer assembly of polyaniline (PANI) and multi-walled carbon nanotube (MWCNT). The protecting effect of polyaniline layers and the electrostatic interaction between positively charged PANI and negatively charged MWCNT were used to alternately assemble homogeneous and stable MWCNTs and PANI mutilayer films on glassy carbon electrode (GCE). The conducting polymer film was prepared by electrochemical polymerization of aniline or its derivatives, whereas MWCNTs were pre-treated with concentrated hydrochloric acid to purify the nanotube and oxidize its end groups. Cytochrome P450 3A4 enzyme was assembled on modified GCE by either cross-linking with glutaraldehyde in the presence of bovine serum albumin (BSA) or potentiostatic deposition at +600 mV vs. Ag/AgCl. The PANI-on-MWCNTs nanobioelectrode had exceptional anti-interference and superior charge transduction properties. Electron exchange characteristics of the bioelectrode were studied by anaerobic and aerobic dc-voltammetry as well as frequency-modulated ac-voltammetry. The biosensor kinetic dynamics were optimised with known standard substrates and inhibitors of CYP3A4. Amperometric capture of the biosensor's metabolic profile of the antiretroviral drug ritonavir is presented.End of abstract text

# Nano-electrochemistry on the AFM-Tip applied to live cells

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Combined AFM/SECM (Atomic Force/Scanning Electrochemical Microscopy) probes provide *simultaneously* topographical and laterally resolved electrochemical information at the sample surface during AFM imaging [1,2]. Predominantly, thin-film chemical vapor deposition (CVD) and sputter techniques along with focused ion beam (FIB) milling originating from microelectronics are utilized for the fabrication of AFM tip-integrated frame, ring, and disk electrodes. The result is a defined electroactive area recessed from the apex of the original AFM tip. Hence, simultaneously measured Faradaic currents and topographical information can be correlated in space and time.

The application of integrated AFM-SECM probes can be extended by surface modification of the tip-integrated electroactive area resulting in combined AFM-micro-/nanosensors - ranging from integrated amperometric microbiosensors (e.g. for glucose, ATP) to potentiometric sensors. Immobilization schemes for enzymes providing reproducible modification of miniaturized electrodes will be presented [3]. Due to the achieved current-independent positioning of the integrated sensor, laterally resolved information on electroactive and -inactive processes can be obtained at the solid/electrolyte interface during AFM imaging.

[1] J. V. Macpherson, P. R. Unwin, Anal. Chem. 2000, 72, 276-285.

[2] C. Kranz, G. Friedbacher, B. Mizaikoff, A. Lugstein, J. Smoliner, E. Bertagnolli, Anal. Chem. 2001, 73, 2491-2500.

[3] A. Kueng, C. Kranz, A. Lugstein, E. Bertagnolli, B. Mizaikoff, Angew. Chem. Int. Ed. 2005, 44, 3419-3422.

# Multi-color Electrochromism of Nanoparticles of Prussian blue and Its Analogues

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We developed nanoparticles of Prussian blue (PB) and that of its analogues (PBA). The nanoparticles are covered with protecting molecules to disperse in solvents. As a result, various conventional coating/printing methods can be utilized in high-quality micro-fabrication to prepare various electronic devices. We have demonstrated electrochromic behavior of thin films of the PB nanoparticles, indicating potential applications for displays, smart windows, and etc.

The particle size of PB nanoparticles that we developed is about 10 – 20 nm, as shown in Fig. 1. These nanoparticles are well dispersed in toluene. With this dispersion liquid, we prepared a thin film on an ITO substrate by spin-coating method. This film exhibits electrochromism, as well as the bulk sample. A color changes from blue to colorlessness occurs reversibly among +1V as –1V, even after 10,000 times operations. A couple of PBA consisting of different transition metals also exhibit electrochromism with different colors.

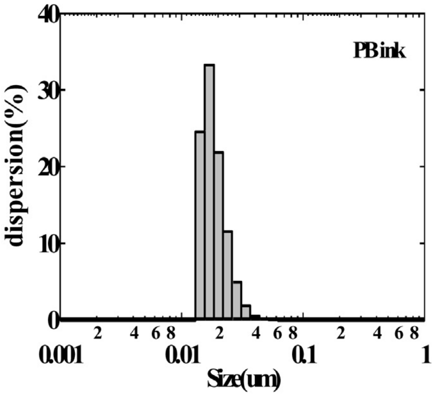

Fig. 1. The particle size distribution of PB in the ink (in toluene)

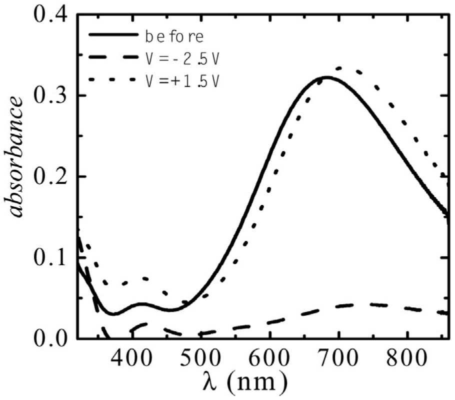

Fig. 2. electrochromic behavior of a thin film of the Prussian blue nanoparticles

# Electrochemical Properties of II-VI Quantum Dot Monolayers at Blocked Electrodes

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The generation of opto-electronic, sensing and photovoltaic systems based on quantum dots (q-dots) requires detailed understanding of the electronic communication between the dots and macroscopic electrodes. Several approaches have been considered for studying charge transport across q-dots assembled at electrode surfaces, most notably low-temperature scanning tunnelling spectroscopy [1]. On the other hand, q-dot mediated electron transfer in an electrochemical configuration remains essentially unexplored. This issue requires a rational experimental design in order to minimise the direct electron transfer from the probe to the electrode surface and the electrochemical decomposition of the q-dots. In the present contribution, we shall describe our initial investigations on the dynamics of electron transfer mediated by II-VI dots assembled at modified Au electrodes.

Water-soluble CdTe and CdSe dots protected by 3-mercaptopropionic acid (MPA) were prepared by a two-step synthesis protocol [2]. Careful tuning of the synthesis conditions allows controlling the average dot radius in the range of 1.70 to 2.44 nm. The position of the valence band edge of the dots, with respect to the reference electrode, was estimated from current-potential measurements of the colloidal solutions using a rotating disc electrode [3]. The relative position of the conduction band edge was calculated from the optical band gap of the q-dots.

The q-dot monolayer on Au electrodes was generated by electrostatic adsorption on polyelectrolyte modified surfaces. Au electrodes were sequentially modified by a self-assembled monolayer of 11-mercaptoundecanoic acid (MUA) and an ultrathin layer of poly-L-lysine (PLL). We have shown that the MUA-PLL film strongly blocks the electron transfer process involving the ferri/ferrocyanide couple [4]. The electrochemical properties of the 2D assemblies were investigated by cyclic voltammery and electrochemical impedance spectroscopy. The experimental data are rationalised in terms of the dynamics of electron tunnelling through the q-dot monolayer and the relative position of the narrow energy bands of the nanocrystals.

References
1.- E.P.A.M Bakkers et al., *Nanolett.*, **1** (2001) 551
2.- H. Zhang and B. Yang, *Thin Solid Films*, **418** (2002) 169
3.- G. Kissling, et al., poster presentation, ISE Spring meeting, Dublin, 2007.
4.- J. Zhao et al., *J. Phys. Chem. B*, **109** (2005) 22985

# Single molecule electronic behaviour of α, α’–bis(6–mercaptohexyl)oligothiophenes and related compounds.

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Over recent years several techniques have emerged designed to study nanoscale electronic junctions containing as little as a single molecule[1-6]. One such method developed by Haiss et. al. was used to show conductance increase in a viologen molecule by one electron reduction of the centre group[3]. A theoretical description of the process treats the central bipyridinium unit like a barrier indentation to the tunnelling charge[7]. Our work poses the question ‘what are the boundary conditions for a group to behave as a barrier indentation?’ We have used the so called I($s$) and I($t$) techniques[2] to investigate the behaviour of α, α’–bis(6–mercaptohexyl)oligothiophenes, in which the redox active viologen moiety is replaced by a simple arene unit. We show here that the simple arene unit is capable of acting as a barrier indentation. It is well known that the conductance of simple alkanedithiols decreases exponentially with length. However, we find that the conductance of α, α’–bis(6–mercaptohexyl)oligothiophenes does not decrease with the length of the oligothiophene. Going from mono to bi thiophene units we see more than a two fold increase in conductivity, and from bi to quinque the conductivity does not decrease.

1. Cui, X. D. *et al*. Reproducible measurement of single-molecule conductivity. *Science* **294,** 571–574 (2001).
2. Haiss,W. *et al*. Measurement of single molecule conductivity using the spontaneous formation of molecular wires. *Phys. Chem. Chem. Phys.* **6,** 4330–4337 (2004).
3. Haiss,W. *et al*. Redox state dependence of single molecule conductivity. *J. Am. Chem. Soc.* **125,** 15294–15295 (2003).
4. Xu, B. Q. & Tao, N. J. J. Measurement of single-molecule resistance by repeated formation of molecular junctions. *Science* **301,** 1221–1223 (2003).
5. Weber, H. B. *et al*. Conductance properties of single-molecule junctions. *Physica E* **18,** 231–232 (2003).
6. Reichert, J. *et al*. Driving current through single organic molecules. *Phys. Rev. Lett.* **88,** 176804 (2002).
7. Submitted to *J. Phys. Chem,* J Ulstrup et. al.

# Haem Protein in Nonaqeous Solvents: Electrochemistry and Spectroscopy

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Enzymes such as trypsin and subtilisin are now widely used as efficient catalysts in nonaqueous solvents. The use of redox enzymes is much less widespread, mainly due to their instability which arises from the need for an exogeneous oxidant, typically hydrogen or alkyl peroxides. We are interested in examining the properties of haem proteins with a view to using these proteins as biosensors and biocatalysts in nonaqueous solvents. We are examining the electrochemical and biocatalytical properties of hemin and of the haem proteins, myoglobin, haemoglobin, cytochrome c, horseradish peroxidase and chloroperoxidase in nonaqueous solvents. The thermoodynamics of reduction of the haem moiety of these proteins in a range of solvents indicates that the each protein and each solvent have to be examined independently, with no discernible trends evident between solvents. When the haem is noncovalently bound to the protein, it is apparent that the haem is partially removed from the haem binding pocket, indicating the possibility of using these proteins as biocatalysts. Chloroperoxidase was immobilised on to a solid support and was re-used 20 times without loss of activity.

# Layered Double Hydroxides-Enzyme nanohybrid materials applied to biosensor development

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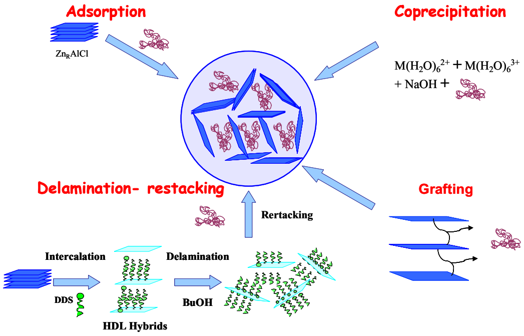
Bioinorganic hybrid materials constitute a new generation of materials, at the interface of biology and material science, able to display functionalities as complex as that of natural systems such as drug vectorisation, target delivery system or sensing properties. Among these bioinorganic structures, enzyme-layered double hydroxides nanohybrid materials are under investigation for the elaboration of electrochemical biosensors.
Due to their anionic exchange properties, wide range of chemical composition and versatile structural and textural properties, Layered Double Hydroxides (LDH) are very appropriate materials for the immobilization of enzymes which often bear an overall negative charge. Various soft chemistry processes such as adsorption, delamination/restacking, chemical grafting and coprecipitation methods have been used to synthesize these new active bioinorganic LDH-Enzyme nanohybrid materials (Scheme):



Scheme : Different methods to prepare LDH-Enzyme nanohybrid materials

These immobilization procedures have been applied with different enzymes, such as tyrosinase, alkaline phosphatase, laccase, nitrite reductase for electrochemical biosensors development. These biosensors have been applied to the amperometric detection of water pollutants such as phenols, cyanide, arsenate, nitrite.

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# A Spectroelectrochemical Approach to Complex Membrane Proteins

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Membrane proteins such as the cytochrome c oxidase, the bacterial reaction center and the light harvesting complex, genetically engineered with his-tags, to be immobilized in strict orientations on metal or oxidic surfaces are reconstituted *in situ* in bilayer lipid membranes.[1] They can thus be investigated by a combination of electrochemistry and vibrational spectroscopy methods. A kinetic analysis of electron transfer through all four redox centers of the cytochrome c oxidase from *Rh. sphaeroides*, for example, was performed by electrochemistry, controlled by surface-enhanced resonance Raman (SERRS). The reaction was initiated by bioelectronic coupling with an exceptionally high rate constant ($>4000\ s^{-1}$), when the enzyme was immobilized with the cytochrome c binding site directed towards the electrode. Consecutive electron transfer steps are thus investigated under physiologically relevant conditions, employing fast scan cyclic voltammetry.[2,3] Evidence for the direct ET as well as for the structural integrity of CcO was derived from Soret band excited SERRS as a function of potential, taken at strictly *anaerobic* conditions. The characteristic marker band region ($1300$-$1750\ cm^{-1}$) is very sensitive to the integrity of the heme structure and its protein environment, and provides information on the redox state, the ligation, spin and coordination state of the heme $a/a_3$ structure. Conformational transitions as a consequence of electron transfer reactions were then followed by electrochemically triggered time resolved surface-enhanced infrared reflection absorption spectroscopy (trSEIRAS). Time constants down to μs could be obtained and analysed in terms of the enzymatic cycle. Investigations carried out under *anaerobic* and *aerobic* conditions revealed information about proton transport coupled to electron transfer. With the cytochrome c oxidase in the orientation mentioned above, protons are transported into the interstitial space between the lipid membrane and the electrode, where they are reduced to hydrogen. Proton transfer can thus be investigated separately from electron transfer to reveal mechanistic information of the enzymatic cycle. Cytochrome c oxidase in the inverted orientation, with the cytochrome c binding site pointing into the bathing solution, was activated by cytochrome c. Under *aerobic* as compared to *anaerobic* conditions, oxidised cytochrome c was shown to give rise to catalytic cathodic currents due to the repeated turnover of the enzyme. Cytochrome c in the reduced form under otherwise the same conditions, gave an amplified anodic current which can only be explained in terms of an acceleration of electron transfer in the catalytic center. Impedance spectroscopy was then used to investigate proton transfer coupled to electron transfer activated by reduced cytochrome c and also to characterise the electrochemical properties of the biomimetic protein/lipid bilayer structure[1].

[1] F. Giess, M. Friedrich, J. Heberle, R. Naumann, W. Knoll, *Biophys. J.* **87**, 3213 (2004)
[2] E. Laviron, *J. Electroanal. Chem.* **101**, 19 (1979)
[3] L. J. C. Jeuken, J. P. McEvoy, F. A. Armstrong, *J. Phys. Chem. B.* **106**, 2304 (2002)

# DNA Sensors in Selectively Modified Nanoporous Electrode Structures

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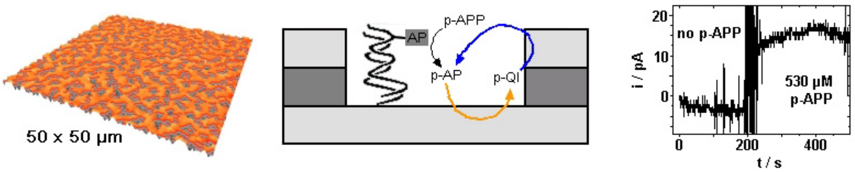
Recently, a novel nanoporous electrode structure was introduced [1,2]. Electrodes consist of layered metal/insulator/metal assemblies with the top metal and insulator layers being porous to form nanopores with separately addressable electrodes at pore bottoms and rims. Electrode separation as defined by the insulator thickness is typically 100-200 nm. The small electrode separation enables high signal amplification by means of redox recycling [2].



*AFM image of an ensemble of nanopores, schematic of DNA-detection amplified by means of redox recycling, and response of a model DNA sensor using disk ultramicroelectrodes*

To employ the nanoporous structures in biosensor applications, a selective modification of nanopores with biological recognition elements is necessary. In this contribution, we will focus on the use of thiol chemistry to immobilize probe DNA selectively within the nanopores at the bottom electrode. Probe oligonucleotides were constructed bearing thiol side chains. Using different applied potential for the bottom and top electrode the formation of the Au/thiol monolayer predominantly occurs at the bottom electrode leaving the top electrode non-modified. Initially, correspondingly modified Au micro-electrodes were used as model sensors. Redox cycling after binding of a complement-tary, alkaline phosphatase (AP) labelled target oligonucleotide was evaluated in the presence of p-aminophenylphosphate (p-APP) using scanning electrochemical micros-copy (SECM) in the feedback mode with the microelectrode positioned in closed distance to a bare Au electrode. Optimization of the amplified DNA sensor using the above mentioned nanopore electrode structures will be demonstrated.

[1] M. Stelzle and W. Nisch, WO 02/084272 A2 (**2001**), NMI: PCT
[2] S. Neugebauer, U. Müller, T. Lohmüller, J. P. Spatz, M. Stelzle, W. Schuhmann, *Electroanalysis* 18 (**2006**), 1929

# Electrochemiluminescent Metallopolymers for Detection of Biological Analytes

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**Electrochemiluminescence (ECL) represents a sensitive and potentially selective approach to detecting biomolecules ranging from DNA to protein and antibody biomarkers.[1] Our priority is to develop "reagentless" systems where the luminescent species is immobilised directly on an electrode surface. ECL production is highly dependent upon the rate of charge transfer ($D_{CT}$). Non-conjugated metallopolymers that have previously been reported for ECL production suffer from a relative slow rate of charge transfer compared to metallopolymers that support a $\pi$ conjugated network along the polymer backbone.[2]**

**Here, we report on the development of ruthenium containing conjugated metallopolymers with enhanced rates of charge transfer for use in ECL production. These metallopolymers have been developed with conjugated backbones which have previously been shown to aid in the communication between adjacent metal centres. The electrochemiluminescent, electrochemical and photophysical properties of the metallopolymers have been extensively studied and are reported herein.**

[1] Knight, A. W.; Greenway, G. M. *Analyst* **1994**, *119*, 879-890

[2] C. G. Cameron and P. G Pickup *Chemical Communications* **1997**, *11*, 2253.

# Novel Electroactivities of Nanostructured Metallophthalocyanine – Single-Walled Carbon Nanotube Arrays at Gold Surfaces

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Redox-active transition metallophthalocyanine (MPc) complexes are well known powerful electrocatalysts for the design of electrochemical sensors [1]. Single-walled carbon nanotubes (SWCNTs) exhibit excellent electrical conductivity. Integration of CNTs and redox-active MPc complexes could revolutionize their application in electroatalysis and sensing. This paper will discuss examples of the rational integration of SWCNT with MPc complexes via layer-by-layer self assembly method [2]. The success of this technique was proved by XPS, AFM, RAMAN and EIS studies. Comparative electron transfer capabilities of SWCNT, MPc and SWCNT-MPc will be discussed.

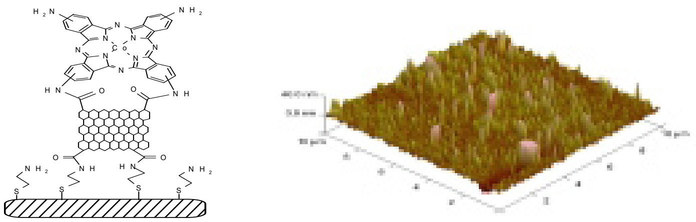

Fig. 1: Nanostructured electroactive SWCNT-CoTAPc arrays on gold surface [2].

References

[1] K.I. Ozoemena, T. Nyokong, In *Encyclopedia of Sensors* (Edited by C. A. Grimes et al), ASP, California, **2006**, Vol.3, Chapter E, pp.157– 200. [2] K.I. Ozoemena, T. Nyokong, D. Nkosi, I. Chambrier, M.J. Cook, *Electrochim. Acta* **2006** (in press).

# Self-Assembled Monolayers at Electrodes in DNA and Protein Analysis

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Faradaic signals of DNA and RNA are electrochemically irreversible, occurring at highly positive or negative potentials. Electroactive labels, including nanocrystals and nanoparticles, were introduced into DNA to obtain signals closer to the potential of zero charge and/or to increase the sensitivity and specificity of the analysis (1). Osmium (VIII) and Os(VI) complexes can be used for end-labeling of DNA and RNA. Ss oligodeoxynucleotides (ODN) probes immobilized on solid surfaces are commonly used in DNA hybridization sensors. Direct linkage of thiol-end-labeled ODNs (HS-ODNs) at gold surfaces, facilitating formation of DNA self-assembled monolayer (SAM), is one of the most frequently used ways of DNA immobilization in these sensors. Such monolayers resemble the well-known self-assembly of alkanethiols on gold surfaces. Recently we have shown that HS-ODNs form self-assembled monolayers (SAMs) at mercury electrodes providing signals due to (a) reduction of bases and (b) reduction of the Hg-S bond (2). Changes in voltammetric signals due to cytosine and Hg-S bond reduction indicated changes in positioning of the HS-$(TTC)_7$ molecules at the electrode with increasing HS-$(TTC)_7$ concentration from lying flat with respect to SAMs, to upright-standing molecules. Densely packed SAM behaved as an insulator not allowing electron transfer between $[Ru(NH_3)_6]^{3+}$ and the electrode. Different adsorption modes of thiolated and thiol-free DNAs were observed. We show that electroactivity of some amino acid residues in proteins can be utilized in analysis of proteins important in biomedicine (3). Constant current chronopotentiometry (CPS) with bare and chemically modified electrodes is particularly useful for recognition of changes in protein structures induced by denaturing reducing and oxidizing agents as well as by single amino acid exchange in proteins important in cancer (3,4). Using CPS and other methods, aggregation of amyloidogenic proteins can be traced. Recently pre-aggregation changes have been discovered by these methods in proteins important in Parkinson‘s and Alzheimer‘s diseases.

1. Palecek E. and Jelen F. (2005): In: Palecek E., Scheller F. and Wang J. (eds.) (2005): Electrochemistry of nucleic acids and proteins. Towards electrochemical sensors for genomics and proteomics. Elsevier, Amsterdam.74-174.
2. Ostatná V. and Palecek E. (2006), Langmuir 22, 6481-6484.
3. Palecek E (2005): In: Ref. 1, pp. 690-750.
4. Ostatná V., et al. (2006), *J. Electroanal. Chem.* 593, 172-178.

# Electrocodeposition of Nickel-Alumina Nanocomposite Films under the Influence of Static Magnetic Fields

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Dispersion coatings are well-known surface finishings. They have a broad range of applications from decorative to functional needs. This flexibility results from various possibilities of combinations of matrix materials and dispersed phases. As there is an ongoing trend of miniaturization the dimensions of codeposits have to shrink which makes the use of nano-scaled particles mandatory. That is why the focus is shifting from the micro particles to nano particles. This comes along with new difficulties. Small particles have high surface energies and will agglomerate and sediment readily in technical electrolytes.

Thus there is a strong need for sophisticated preparation techniques which can produce thin dispersion coatings containing some volume percent of nano-scaled particles. There have been several studies which show that the deposition rate of metals and alloys can be increased in the presence of a magnetic field. Therefore we decided to superimpose a static magnetic field (up to 0.7T) during the electrocodeposition of 13 nm alumina particles in a nickel matrix. As alumina is a diamagnetic material a magnetic field should have little or no effect on the particles themselves. Therefore the particles have been coated with a nickel shell to make them ferro- or at least super-paramagnetic which allowed to bring relatively strong forces into play. These coated particles should move in a gradient of a magnetic field which could be aligned perpendicular or parallel to the current.

The dispersion coatings were deposited galvanostatically onto a gold electrode of a quartz crystal microbalance. This allowed us to monitor the mass change of the layers in situ. The particle content was then calculated from the current efficiency and cross-checked with EDX-analysis.

The experiments showed that perpendicular fields enhance the incorporation of uncoated particles by 10 % $T^{-1}$ while there was virtually no effect on the coated particles. Parallel fields can increase the particle content of magnetic particles (coated) while the content of non-magnetic particles (uncoated) is unaffected. These results can be explained by magnetohydrodynamic effects in the case of uncoated particles in perpendicular fields. The magnetic field induces convection because of the Lorentz force which stabilizes the suspension and transports more particles to the surface. The coated particles seem to be mainly transported by magnetophoretic forces along the gradients of the magnetic field the sources of which are manifold in our experimental setup.

# Synthesis, characterization and electrochemistry of redox-modified silica particles on platinum electrode surfaces

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The work in our group, involving nonporous redox-active silica particles (< 200 nm in diameter) immobilized on platinum electrodes, shows how active centres can be accessible for a redox process when immobilized on a non-conducting substrate[1]. Ferrocene molecules covalently bound to the silica surface are oxidized and the resulting ferricinium ions reduced even in the absence of a direct contact with the electrode surface. The electron transfer occurs via electron hopping between neighbouring ferrocene molecules over the whole particle surface. Cyclic voltammetry is used to determine the kinetics of the electron transfer and the accessibility of the ferrocene units.

The large variety of materials useable as the non-conducting substrate gives a wider choice for the immobilization of a given redox system on electrodes. As an example we describe the modification of a silica surface with silicon hydrides and with carboxylic groups for the immobilization of redox molecules[2].

The bonding principle demonstrated for ferrocene should also be applicable for other redox active compounds. For example, the immobilization of nitrate reductase on electrode materials for the preparation of nitrate biosensor has promising commercial applications[3]. However the activity and stability of the enzyme in solution is mostly lost once immobilized on an electrode surface. To overcome this problem, the enzyme could be immobilized indirectly on the electrode via a non- conducting substrate better adapted to the enzyme.

1. A. Budny, F. Novak, N. Plumeré, B. Schetter, B. Speiser, D. Straub, H.A. Mayer and M. Reginek, Langmuir *51*, 10605 - 10611 (2006)
2. N. Plumeré and B. Speiser, Electrochim. Acta, submitted.
3. G. G. Barbier and W. H. Campbell, Protein Expr. Purif. *37*, 61-71 (2004)

# Electrochemical Detection of Biological Reactions Using a Novel Nano-Bio-Chip Array

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We developed an innovative electrochemical ‘lab on a chip’ system that contains an array of nano volume electrochemical cells on a silicon chip. Each of the electrochemical cells can be monitored simultaneously and independently, and each cell contains three embedded electrodes, which enable performance of all types of electrochemical measurements. The integration of living organisms on an electrochemical array chip that can emulates reactions of living organisms and sense essential biological functions have never been demonstrated before. In order to show the wide range of applications that can be beneficial from this device, biological components including chemicals, enzymes, bacteria and bio-films were integrated within the nano-chambers for various applications. During the measurement period the bacteria remained active, enabling cellular gene expression and enzymatic activity to be monitored on line.

The miniaturized device was designed in two parts to enable multiple measurements: a disposable silicon chip containing an array of nano-volume electrochemical cells that are housing the biological material, and a reusable unit that includes a multiplexer and a potentiostat connects to a pocket PC for sensing and data analysis [1].

This electrochemical 'lab on a chip' was evaluated by measuring various biological reactions including the microbial current response to toxic chemicals. These bacteria were genetically engineered to respond to toxic chemicals by activating cascade of mechanisms, which leads to the generation of electrical current. A measurable current signal, well above the noise level, was produced within 5 minutes of exposure to phenol, a representative toxicant.

The 'Lab-on-a-chip' system was also employed for sensitive and high-throughput detection of cancer cells, in response to differentiation therapy. Cancer cells were treated with different differentiation therapy drug agents, and cells response to the drugs was measured simultaneously and on line. This microarray technology provides the ability to test on line multi-drug agents, and tailored effective therapy to the individual.

In Summary, We demonstrate sensitive measurements on extremely small samples (less than ~15 cells) and no special cell treatment is required prior to the insertion into the chip.

References

1. R. Popovtzer, et al; Novel Integrated Electrochemical Nano-Bio-Chip for Toxicity Detection in Water Nano Letters 2005, 5, 1023 - 1027

# Use of crystalline proteins for templated electrodeposition

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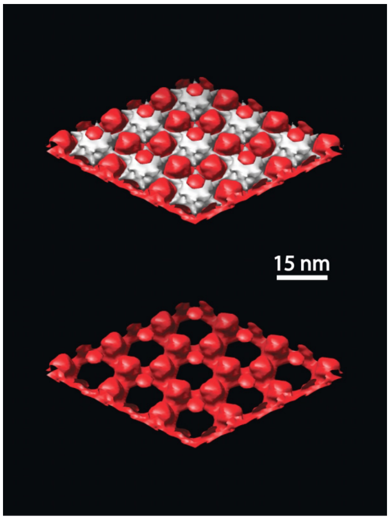

Three dimensional transmission electron microscopy (3D-TEM) is used to characterize the structure of materials electrodeposited through the hexagonally-packed intermediate (HPI) layer protein from *D. radiodurans.* The crystalline protein monolayers were prepared on unique TEM-compatible electrodes using methods and materials described previously.[1-3] Moderate pH electrodeposition baths (4 pH 11) were necessary to preserve the crystalline protein structure. The TEM tilt series data and 3D reconstruction was performed at the National Resource for Automated Molecular Microscopy at Scripps. The adjacent figure shows reconstruction data for cuprous oxide electrodeposited through the crystalline protein monolayer. The top image shows electron density contours that represent the inorganic deposit (red) and the protein template (white). The electrodeposited material grows through the openings in the protein as a hexagonal array, with the larger cuprous oxide particle displaying 3-fold symmetry and smaller particles appear on top of the 6-fold protein sites. The bottom image shows the 3D architecture of the electrodeposited material by itself, with the protein removed. One sees that each of the large cuprous oxide particles sits on a thin, fully interconnected hexagonal lattice on the substrate. This work demonstrates that the 3D pore structure in HPI-layer protein is fully solvent accessible. Moreover, we show that electrodeposition of complex inteconnected structures is possible below 10 nm, augering well for continued down-scaling of the complex 3D interconnect structures in VLSI.

1. D.B. Allred, M. Sarikaya, F. Baneyx, and D.T. Schwartz, Electrochemical Nanofabrication using crystalline protein masks, *Nano Lett.* **5**, 609-613 (2005).
2. D.B. Allred, M. Sarikaya, F. Baneyx, and D.T. Schwartz, Bacterial surface layer proteins for electrochemical nanofabrication, *Electrochim Acta.* submitted.
3. D.B. Allred, M.T. Zin, H. Ma, M. Sarikaya, F. Baneyx, A.K.-Y. Jen, D.T. Schwartz, Direct Nanofabrication and Transmission Electron Microscopy on a Suite of Easy-to-Prepare Ultrathin Film Substrates, *Thin Solid Films*, accepted.

# Particle Size and Substrate Effects in Electrocatalysis: Carbon and Titania Supported Gold Particles

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PVD methods have been used to investigation of particle size and support effects on electrocatalysts. The kinetics of oxygen reduction and CO oxidation at gold particles on both carbon and sub-stoichiometric titania is described for mean particle diameters in the range 1.4 nm to 7 nm. There is a strong particle size effect on the catalytic activity of the gold centres supported on titania or carbon for oxygen reduction. Loss of activity is observed for very small centres with diameters below 2.5 nm and the trend implies that centres below 1 nm are totally inactive. In the case of titania supported Au particles, a maximum in oxygen reduction activity is also observed at particle sizes of ca. 3nm. We also shown that the electrocatalytic oxidation of CO is promoted on titania supported gold particles, and that the optimum particle size for the reaction is ca. 3nm.

# Kinetics of oxygen reduction on gold nanoparticle/multi-walled carbon nanotubes hybrid electrodes in acid solution

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The electrochemical reduction of oxygen has been studied on gold nanoparticle/multi-walled carbon nanotubes (AuNP/MWCNT) modified glassy carbon (GC) electrodes in 0.5 M $H_2SO_4$ using the rotating disk electrode (RDE) technique. The oxygen reduction behaviour of these electrodes was compared with that of a bulk gold electrode. Carbon nanotubes (CNTs) can be used as a support material for various catalysts and for this reason their electrocatalytic properties towards $O_2$ reduction are of great fundamental and practical importance. In order to test the support material the $O_2$ reduction behaviour of oxidatively pre-treated and untreated MWCNTs modified GC electrodes was compared. Untreated MWCNTs show improved electrocatalytic properties towards $O_2$ reduction in acid media than those of pre-treated MWCNTs. This effect is caused by catalyst impurities, which remain in the nanotubes prepared by CVD and can be largely removed by acid treatment [1]. The half-wave potential ($E_{1/2}$) shifted more than 250 mV in the negative direction upon MWCNTs treatment in acids. It is shown that chemical oxidation of MWCNTs increases the coverage by oxygenated species on nanotubes, but these groups do not enhance the rate of $O_2$ reduction in acid solution. The results obtained clearly demonstrate the effect of impurities containing in MWCNTs on the kinetics of $O_2$ reduction. These aspects are important for electrocatalytic and electroanalytical applications of CNT modified electrodes.

The AuNP/MWCNT catalysts were prepared employing a published procedure [2]. The AuNP/MWCNT catalyst showed a remarkable electrocatalytic activity towards $O_2$ reduction in acid media. The value of $E_{1/2}$ for $O_2$ reduction on the AuNP/MWCNT catalyst is shifted by *ca* 50 mV to more positive potentials as compared to that of a polished Au electrode. The RDE results reveal that the reduction of oxygen proceeds by a two-electron pathway at low overpotentials. The reduction of $O_2$ on the hybrid electrode overlapped with that of the untreated MWCNTs modified GC electrode. The results obtained indicate that the substrate plays an important role in the $O_2$ reduction mechanism.

Work is in progress to use new methods for the preparation of the AuNP/MWCNT catalysts and the electrochemical properties of the hybrid electrodes will be discussed.

**References**

[1] G.G. Wildgoose, C.E. Banks, R.G. Compton, *Small* 2 (2006) 182.
[2] M. Zhang, L. Su, L. Mao, *Carbon* 44 (2006) 276.

# Development of an electrochemical immunosensor for West Nile virus

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West Nile virus (WNV), a member of the family Flaviviridae, is a single-stranded positive sense RNA envelope virus. It is an important cause of epidermic viral encephalitis that has since spread through North America. The hosts of this virus are birds and transmission to humans involves the mosquito *Culex* species, which serves as the vector. So far, no vaccine is available for humans. Hence, frequent surveillance of WNV activity in birds and mosquitoes is essential as a preventive measure to human infection. The domain III of the WNV glycoprotein E carries epitopes eliciting antibodies and can exist independently in a stable conformation. Hence WNV-DIII serves as an attractive target antigen, and has been used for WNV detection using conventional enzyme-linked immunosorbent assay (ELISA) technique. Herein, we describe an alternative electrochemical method based on nanoporous alumina modified platinum electrode. The adsorption of IgM along the pore channel walls and the specific binding of WNV-DIII to the immunoglobulin M (IgM) layers afford blocked channels, reducing the sensor response towards an electroactive redox couple. A calibration curve relating the change in faradaic currents to WNV-DIII concentrations in the analyte solution is optimized through the study of variables involving IgM concentrations, pH, ionic strength and overlaid alumina pore sizes.

# Biological and Chemical Sensing Using Transmission Localized Surface Plasmon Resonance (T-LSPR) Spectroscopy

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Gold and silver island films prepared by metal evaporation 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. We have carried out a detailed study of Au and Ag island films, characterized using AFM, high-resolution SEM and cross-sectional TEM, thus providing rational control over the optical properties. Metal island films with multilscale roughness were achieved by a three-step procedure, i.e., evaporation of an island film, surface modification with a self-assembled monolayer, and evaporation of a second island film. Structural reshaping of island films, enabling tuning and optimization of their optical properties, was achieved by thermal, chemical and electrochemical treatments.

The SP absorption band (intensity and wavelength of maximum absorbance), measured in the transmission mode, changes upon binding of various molecules to the surface. This new method of transduction of surface binding events to optical signals was termed Transmission Localized Surface Plasmon Resonance (T-LSPR) spectroscopy. The refractive index sensitivity and distance dependence of the T-LSPR signal were studied using variable liquid media and a coordination-based self-assembled multilayer of a variable thickness. The optical response of an optimized Au island film remained nearly constant at distances up to >15 nm from the Au island surface, providing flexibility in the design of T-LSPR based sensing interfaces.[1] Encapsulation of Au island film into ca. 1.5 nm continuous silica shell prevents any change of the island shape providing conditions when optical response is sensitive only to changes in the effective dielectric constant of immediate environment.[2]

Protein recognition interfaces were prepared by stepwise functionalization of Au island films (5 nm nominal thickness) to carry carboxylate functionalities that covalently link to the amino groups of proteins. Antibody-derivatized Au island films prepared in this manner were used as a recognition surface for selective sensing of antigen binding, distinguishing specific and nonspecific interactions by means of an array of four T-LSPR transducers.

Single-stranded (SS) DNA oligomers modified with a disulfide group at the 5’ end were immobilized on Au island surfaces. The resulting interface was used for sensing the binding of the complementary strand, distinguishing specific (complementary) and nonspecific (non-complementary) interactions.

The applicability of Au island film for gas recognition was demonstrated by exploiting the different sensitivity of thin polymer coatings on Au island films to vapors of different solvents.

# Electrochemical aspects of nanostructure display technology based on titanium dioxide-attached viologen chromophores.

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Viologen ($V^{2+}$) molecules, derivatized with phosphonic acid attachment groups can be chemisorbed on nanostructured $TiO_2$ layers of thickness in the range 1-5µm. Such materials, with a surface roughness factor in the range 100-500, have recently attracted a considerable interest, notably in the domain of dye-sensitized electrochemical solar cells, but also in electrochromic and photoelectrochromic devices. Our particular interest stems from the fact that colorless viologen $V^{2+}$ is reversibly reduced to the strongly coloured cation radical species $V^{+}$•, usually violet, blue or green, which also remains chemisorbed. Both $V^{2+}$and $V^{+}$• remain attached to the electrode upon multiple redox cycling. At the peak of the colouration spectrum a transmittance below 1% is routinely observed. Further reduction leads to the doubly-reduced $V^0$ form of a pale yellow colour, which is to be avoided for efficient electrochomic operation by a judicious selection of the electrode potential.

The above results suggest the successful use of viologen dyes to electrochromic displays. Such devices can been constructed with a viologen/$TiO_2$/ITO glass negative electrode, a porous doped tin oxide positive electrode, whose operation is based on pseudocapacitive charging-discharging, and a liquid electrolyte, aqueous, organic aprotic , ionic liquid or gel based on the above.

The electrochemical techniques of cyclic voltammetry and chronocoulometry have been applied to the characterisation of both the electrochromic negative and the auxiliary positive electrodes, for the former also in the spectro-electrochemical mode. Keynote experimental results will be presented.

Finally data related to complete displays will be elucidated and a comprehensive equivalent circuit simulating device operation at different levels of abstraction will be discussed.

## References :

[1] U. Bach, D. Corr, D. Lupo, F. Pichot, M. Ryan, Adv. Mater. 14 (2002) 846.
[2] D. Corr, U. Bach, D. Fay, M. Kinsella, C. McAtamney, F. O'Reilly, S.N. Rao, N. Stobie, Solid State Ionics 165 (2003) 315.
[3] M. Möller, S. Asaftei, D. Corr, M. Ryan, L. Walder, Adv. Mater. 16 (2004) 1558.

# Nanoreactors in nature: Bioelectrochemical mechanisms

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Nanodevices are molecules or molecular complexes that have clear and specific functions, and are a few nanometers in size. Millions of nanodevices exist in nature, and in this presentation we will discuss a few examples. Natural nanodevices include photochemical, electrochemical, and synthetic nanoreactors. Photosystems I and II, enzymes, enzymatic systems in the citric acid cycle, and carbon fixation in the reductive carboxylic acid cycle are also common nanodevices in nature. Molecular motors such as ATP synthase, myosin, kinesin, DNA helicases, DNA topoisomerase, DNA helixase, RNA polymerase, and bacterial rotary motors are vital nanodevices that serve to regulate biological processes. Molecules in electron transfer chains act as nanorectifiers and nanoswitches. Biological applications for nanodevices include information transfer, molecular computing, mechanosensors, electroreceptors, magnetoreceptors, magnetosomes, neuronal networks, light sensors, and ion channels. Electrochemical multielectron reactions in photosynthesis [1] and respiration [2-5] are evaluated by thermodynamic and kinetic analysis. Kharkats and Volkov [2-4] first presented evidence that cytochromes *c* oxidase reduces molecular oxygen by a synchronous multielectron mechanism without $O_2^-$ intermediate formation. After this pioneering observation, it became clear that the first step of oxygen reduction is two-electron concerted process. The energy for the $H^+$-pump of cytochrome oxidase is liberated in the last two steps of water formation when the third and forth electrons are added independently of the reaction pathway. Electrochemical principles govern many biological properties of organisms such as the generation of electric fields and the conduction of fast excitation waves. These properties are supported by the function of a variety of natural nanodevices. Ionic channels, which serve as natural nanodevices, control the plasma membrane potential and the movement of ions across membranes; thereby, regulating various biological functions. In plants, excitation waves are possible mechanisms for intercellular and intracellular communication in response to environmental changes [5]. The role of electrified interfaces of plasma membranes in signal transduction is discussed as well.

1. A.G. Volkov, Bioelectrochem. Bioenerg. 21(1989) 3.
2. Yu.I. Kharkats, A.G. Volkov, Biochim. Biophys. Acta 891 (1987) 56.
3. Yu.I. Kharkats, A.G.Volkov, Bioelectrochem. Bioenerg. 22 (1989) 91.
4. Yu.I. Kharkats, A.G. Volkov, Analytical Sci. 14 (1998) 27.
5. A. G. Volkov and C. L. Brown, in C. S. S. R. Kumar (Ed.), Nanodevices for Life Sciences, Wiley-VCH, Weinheim, pp. 440-463, 2006.

# Morphological evolution of polycrystalline Platinum during electrochemical roughening

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Platinum is still considered as the most important catalyst material for polymer electrolyte fuel cells (PEFCs), due to its unique catalytic activity. The structure of Pt surface has a strong influence on its electrochemical reactivity [1]. An interesting morphologic evolution process was observed on a polycrystalline platinum electrode surface during electrochemical roughening (i.e., by cycling intensively between the potentials for hydrogen and oxygen evolution) in sulfuric acid electrolyte [2]. This process was started form a polished polycrystalline platinum electrode and could be divided into 4 stages. First, the Pt electrode surface seemed to be covered by small crystalline islands after a period of cycling. At the second stage, rod like structures, which are named “backbones”, appeared on the electrode surface. After that, some saw-like structures at nanometer scale, which are referred to as “needles”, started to grow along side the backbone. At the final stage, the full-fledged morphology contains a backbone in the center and one or two rows of needles at the side. According to its appearance, the structure is named “feather like morphology (FLM)”. An XPS study indicated that the FLM is composed of Pt(0). SEM and TEM investigations provided both the morphologic details and crystallographic information. We noticed that near the backbone tips, needles are relatively small and tightly bound to the backbone, while away from the tips, needles become bigger and tend to break away from the backbone. It is also worth mentioning that both the backbones and the needles have even finer sub-structures. When a needle is given enough space to grow, its central part could develop into a secondary backbone, and the saw-like structure around the center could become secondary needles. This might be due to the step-wise formation of the FLM. Electron diffraction analysis showed that most of the needles have identifiable crystallographic orientations, and all needles of a feather aligned in one row appear to have the same crystal orientation; while the backbones present complicated ED patterns which are difficult to be interpreted so far. Electrochemical measurements indicate that Pt electrodes roughened by intensive pre-cycling exhibit a stable value for the electrochemically active surface compared with plane electrodes.

[1] N.M. Markovic, P.N. Ross Jr., Surface Science Reports 45 (2002) 117-229

[2] A. Reiner, B. Steiger, G.G. Scherer, A. Wokaun, Journal of Power Sources 156 (2006) 28-32

# Reflection anisotropy spectroscopy of DNA adsorbed at the Au(110)/electrochemical interface.

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Reflection anisotropy spectroscopy (RAS) is a non-destructive optical probe capable of operating on a mille-second timescale that achieves surface sensitivity by measuring the change in polarisation on reflection of normal incidence light from the surface of a cubic crystal. It will be shown that RAS is able to determine the three dimensional orientation of molecules adsorbed at electrochemical interfaces [1] and to monitor the interaction between molecules at such interfaces in real time [2].

The results of recent studies of single stranded and double stranded calf thymas DNA adsorbed at the Au(110)/electrolyte interface will be presented. It will be shown that RAS is able to distinguish between the two forms of DNA and to determine the conditions under which single stranded DNA adsorbes through the phosphate backbone thus leaving the bases expsoed for hybridiastion with the complimentary strand.

1 P. Weightman, G.J. Dolan, C.I. Smith, M.C. Cuquerella, N.J. Almond, T. Farrell, D.G. Fernig, C. Edwards and D.S. Martin, Phys. Rev. Lett. **96** 86102 1-4 (2006)

2 R.LeParc, C.I. Smith, M.C. Cuquerella, R.L. Williams, D.G. Fernig, C. Edwards, D.S. Martin and P. Weightman, Langmuir **22** 3413-20 (2006)

# The Influence of the Electrode Material on the Single Molecule Conductance

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Recently a lot of attention has been directed toward the determination of the effect that the binding group has on the single molecule conductance of a molecular wire between two Au electrodes. [1-4] It has been shown that in ambient conditions and in UHV certain binding groups will not form an electrical connection between the molecular wire and the gold electrode. [4] If binding groups can be found that specifically bind to a certain electrode material, it will be possible to control the way a molecule is located in the gap between two electrodes of different material. This is for example a fundamental requirement to fabricate a molecular wire that acts as a diode. In order to achieve this aim it is, however, essential that the electrical properties of the electrode materials and their interaction with different binding groups is well understood.

Here we show a first study of the effect of the electrode material (Nickel, Platinum and Gold) on the conductance of 1, 4-Benzenedihexanethiol. All measurements were performed using the same experimental conditions, which is under electrochemical control in a Sodium Sulphate aqueous buffer solution at pH of 3. It will be shown that there are distinct differences in the conductance when using different electrode materials.

[1] L. Venkataraman *et al.*, Nano Lett. **6**, 458 (2006)
[2] Z. Li and D.S. Kosov, J. Phys. Chem. B **110**, 9893 (2006)
[3] F. Chen *et al.*, J. Am. Chem. Soc. **148**, 15874 (2006)
[2] M. Kiguchi *et al.*, Appl. Phys. Lett. **89**, 213104 (2006)

# Label-Free DNA-Sensing Using Gan Nanowires Nanosensor

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A novel DNA-sensing system based on GaN nanowires (NWs) is presented coupled with their electrochemical impedance and photoluminescence measurements. GaN, an important III-nitride semiconductor, being a direct and wide band-gap material, were renowned for their potential in optoelectronic application and their inherent bio-compatibility. However, their true application in bio-sensors has been surprisingly absent till date. Simultaneously, one-dimensional (1D) nanostructures have attracted huge interest as potential building blocks for the future nanoelectronic devices. In this report, GaN NWs are used as a transducer for DNA-sensors, by immobilizing ssDNA molecules through covalent binding using organosilane linker (MPTS)*. The immobilization of ssDNA and the subsequent hybridization to dsDNA were confirmed using confocal microscope. Electrochemical impedance measurement showed that interfacial electron-transfer resistance (Ret), from solution to transducer surface, increased significantly when pristine GaN NWs were immobilized with ssDNA, along with a formation of additional semicircle region at lower frequency in Nyquist plot. The unique appearance of double-semicircle region for ssDNA-immobilized NWs, compared to single-semicircle region for pristine GaN NWs, leads to the idea of formation of double-capacitance layer in series. The phenomenon is more prominent by the appearance of double peaks in the plot of phase angle vs. frequency (Bode plot), the second peak, formed after ssDNA-immobilization, showed further increase under the hybridization to dsDNA, and consequently reduces the overall impedance. Moreover, quenching behavior in photoluminescence of the GaN NWs was distinguishable for the ones immobilized with ssDNA and the same hybridized to dsDNA. Both the technique implies the ability of oligonucleotides, immobilized on the NW-surface, to interact with other biomolecules. The dual and label-free sensing capability in impedance and photoluminescence of GaN NWs makes them effective DNA transducers.

# Poster Presentations

# Preparation of Nanosized Electrode Arrays from Self-Assembled Monolayers. Comparison of Experimental and Theoretical Responses and Evaluation of Electroanalytical Detection Limits

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Electrodes with micrometer or nanometer-scale structures have a wide range of applications including photonic materials, high-density magnetic data storage devices, microchip reactors and biosensors. These microstructures behave like an array of microelectrodes (1,2). Microelectrodes have a lot of useful properties due to their very small sizes. They can be made into various shapes, such as disk, spherical, band, cylindrical, and etc. There are several advantages to use microelectrodes over normal electrodes, such as fast establishment of a steady-state signal, high signal to noise ratio, a current increase, and capability to measure solutions of very limited volumes. Microelectrode array has more complex behaviors than the single microelectrodes. One needs to consider the interactions between individual electrodes in the array. The gaps between individual electrodes play a very important roll for the diffusion flux toward a microelectrode array (3).

In this study, we grew small polymer nanostructures electrochemically to the surface of an electrode modified with a two-component self-assembled monolayer. The two-component self-assembled monolayer consists of an electroactive template species (4-Aminothiophenol) and an electrochemically blocking molecule (1-Decanethiol). Polymer structures were formed in the highly localized, surface-confined electrochemistry using these self-assembled monolayers. The surface bound 4-ATP acts as a nucleation site for the growth of polyaniline. It was also studied to show that nanoelectrodes investlgated here can yield electroanalytical detection limits that are lower than detection limits at an equivalent macrosized electrode.

## References

(1) Lin S.-Y.; Chow, E.; Hietala, V.; Villeneuve, P. R.; Joannopoulos, J. D. Science 1998, 282, 274.
(2) Painter, O. Science 1999, 284, 1819.
(3) Wang. J.; Zadeii, J. M. J . Electroanel. Chem. 1888, 249, 339.

# Nanoscale electroless deposition of magnetic alloys.

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Electroless deposition has been utilised to deposit magnetic alloy materials on silicon substrates with nanoscale thickness and in templates to achieve nanotubes of magnetic alloys. Alloys of Co, Ni, Fe and W were deposited and analysed magnetically for applications in such areas as on-chip microtransformers where a high saturation magnetisation and low coercivity is desirable. Standard lithographic patterning facilitated the selective deposition of the magnetic materials. The borane based electroless baths utilised are compatible with standard photoresist materials. Deposition rates ranging from of 50 nm/hr to 5 µm/hr have been achieved for a CoNiFe deposit by varying the reducing agent concentration and the deposition temperature. The analysis to be presented will include SEM, EDX, XRD, magnetic and electrical characterisation.

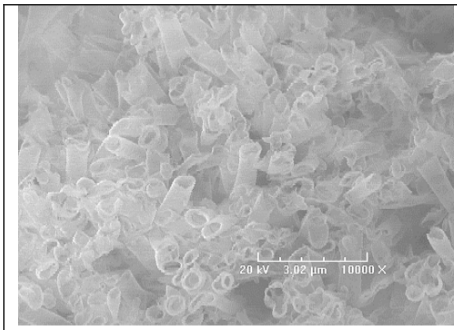

Figure 1. CoNiFe nanotubes ~50nm wall thickness deposited in polycarbonate template

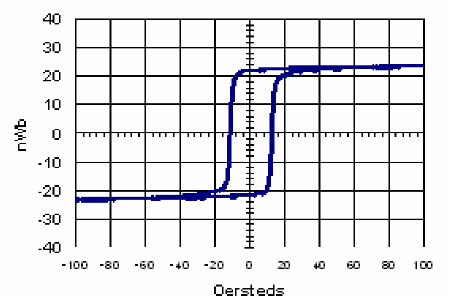

Figure 2. Magnetic characteristics of CoNiFe deposit.

| Sample | Material | Saturation Magnetisation | Coercivity |
|---|---|---|---|
| | | T | (Hc) A/m |
| CoW | $Co_{76}W_{24}$ | 0.620 | 1.4 |
| Co | Co | 1.083 | 2.9 |
| CoFe | $Co_{94}Fe_{6}$ | 1.500 | 18.8 |
| CoNiFe | $Co_{53}Ni_{15}Fe_{32}$ | 2.180 | 11.9 |

Table 1. Magnetic characteristics of the materials investigated

# LB film taste sensor using packaged measuring system

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A Langmuir Blodgett (LB) film taste sensor system using an evaporated Au metal film as an electrode and has a new type of packaged measuring system is reported. The measuring system is changed from conventional glass vessels to a packaged compact epoxy resin body. Sensing films are deposited by dioctadecyldimethyl ammonium bromide (DOABr ), with potassium polyvinyl sulfate ( PVSK） as the polyion complex, using a vertical-dipping LB film fabrication system. The packaged measuring system is compact in size, a low price, and can be mass-produced. Using this sensor, five basic taste substances were clearly discriminated.

Fig.1 shows a schimatic of the measuring system. The measuring body is walled by epoxy resin plates and packaged. A taste sensor with a glass plate is attached to the measuring body which faces 10 mM KCL and taste solution. The taste sensor plate is easy to remove from the body for maintenance and to lengthen the system's lifetime. Quick response and accurate measurement can be obtained because of the close proximity of the taste sensor to the opening of the taste solution. Fig. 2 shows the taste discrimination chart for basic taste substances. Five basic taste substances were clearly identified by detecting the maximum voltage change and titration response time.

References 1) M.Akiya and S.Takafuji, Electrochem 2004, No.59, (2004)

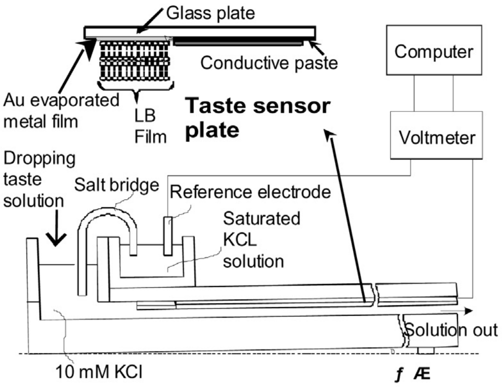

Fig.1 packaged measuring system

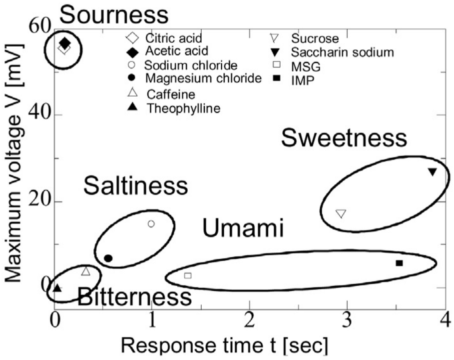

Fig.2 Discrimination chart

# Mixed Polyfluorinated Aminoterminated SAMs as New Platform for Biosensing

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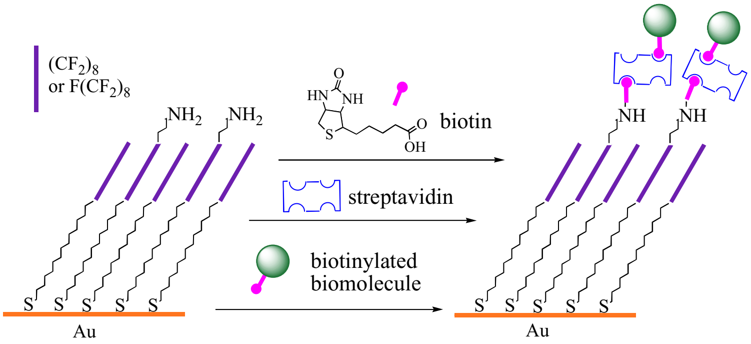
Thin organic layers on solid surfaces have been extensively employed to mimic structures, interfacial phenomena, and processes. One way to prepare such layers is to utilize spontaneous chemisorption of long-chain organosulfur compounds from dilute solutions onto gold forming a so-called self-assembled 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 planed 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 aminopolyfluoroalkanethiol[2], the study of they 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.

# Gold Nanoparticle labels for Enhanced Electrochemical Immunoassay

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Many kinds of nanoparticles, including metal nanoparticles, oxide nanoparticles, semiconductor nanoparticles, and even composite nanoparticles, have been widely used in electrochemical sensors and biosensors. Due to their unique chemical, physical and electronic properties they can be used for example to improve the immobilization of biomolecules, enhance the electron transfer, catalyse electrochemical reactions and for labeling biomolecules, achieving in each of those applications, signal amplifications and increased sensitivity.

The labeling of biomolecules, such as antigen, antibody and DNA with nanoparticles plays an increasingly important role in developing sensitive electrochemical biosensors. Biomolecules labeled with nanoparticles can retain their biofunctionality and interact with their counterparts, and exploiting the electrochemical detection of those nanoparticles, the amount or concentration of analytes can be determined. Dissolution of the nanoparticle labels – mostly metal and semiconductor nanoparticles – and measuring the dissolved ions with stripping voltammetry represents a general sensitive electroanalytical procedure which, however, involves the use of toxic oxidant solution or dangerous strong acids.

In this work, a sensitive electrochemical immunoassay based on gold nanoparticle (AuNP) labels was developed using a direct electrochemical detection of the particles and therefore without the need of the dissolution step. Streptavidin-modified magnetic beads (MB) were used as supporting material to immobilize a sandwich-type immunocomplex with a biotinylated goat anti-human IgG as a primary antibody, human IgG as antigen and analyte and gold-labelled anti-human IgG as a secondary detection antibody. High sensitive voltammetric stripping analysis was performed to directly quantify the specifically captured gold nanoparticles using a graphite-epoxy composite-magnet electrode (GECE-M), that incorporating inside a tiny magnet, sensibly improved the adsorption of gold on the electrode surface. A comparison with the classical spectrophotometric methods (ELISA) employing HRP-labeled antibodies was also performed.

# Constant-distance scanning electrochemical microscopy (SECM) for visualization of glucosedehydrogenase/polymer spot using the enzyme mediated positive feedback mode

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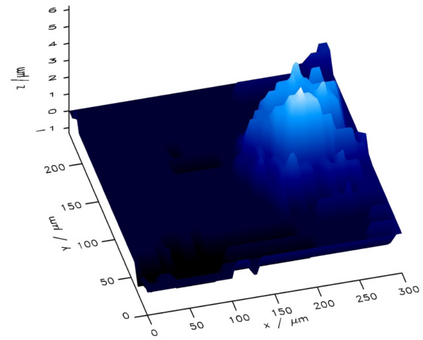
Non-optical and optical shearforce dependent constant-distance SECM was previously applied for high-resolution imaging using sub-µm diameter ultramicroelectrodes [1]. Additionally, we have previously shown that enzyme spots visualized by SECM can be treated as sensor arrays with multiple individual microsensors. In combination with sophisticated mathematical data treatment it was possible to compensate for the impact of interfering compounds or to discriminate between the substrate and the co-substrate of the immobilized enzyme [2]. These studies were performed in constant-height mode of SECM with microelectrodes of 10 or 25 µm using the generator-collector arrangement.

By means of non-optical shearforce detection between the vibrating 500 nmϕ Pt-microelectrode and the sample surface the activity and the topography of a spot of PQQ-dependent glucose dehydrogenase integrated within a polymer could be visualized using the enzyme mediated feedback mode of SECM in presence of ferrocenemethanol and glucose. The topography image of an enzyme spot is shown in Figure 1. However, due to the small electrode surface the simultaneously acquired enzyme activity images exhibited high noise. In contrast, the optical shearforce mode can be used with bigger SECM tips. Local enzymatic activity and topography of the enzyme/polymer spot could be visualized using 7.5 µmϕ carbon fibre disc microelectrodes and ferrocene monocarboxylic acid as mediator. Correlation between the local enzymatic activity and the spot topography has been studied as a basis for biosensor optimization.



[1] a) B. Ballesteros Katemann, A. Schulte, W. Schuhmann. *Chem. Eur. J.* **9**(2003) 2025-2033. b) F. Turcu, G. Hartwich, D. Schäfer, W. Schuhmann *Macromol. Rapid Commun.* **26** (2005) 325-330. c) S. Isik, W. Schuhmann, *Angew. Chem. Int. Ed.* **45** (2006) 7451-7454.
[2] M. Maciejewska, D. Schäfer, W. Schuhmann, *Electrochem. Commun.* **8** (2006) 1119-1124.

# Onset of crystalline order in 1-nonanethiol monolayers deposited from solution

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There seems to be a wide acceptance that thiol self-assembled monolayers exhibit a high degree of structural order, particularly in the case of alkanethiol (HS-$(CH_2)_n$-$CH_3$) SAMs deposited on Au(111). This assumption is well supported from X-ray and helium diffraction, IR and STM studies carried out under either ultrahigh vacuum or ambient conditions, but it turns out to be more controversial when the organic monolayer is in contact with a liquid phase. A number of *in situ* STM and AFM studies of alkanethiol monolayers[1] (with 2 n 17) have visualized ordered domains in the presence of a variety of solvents, which include water, ethanol, 2-butanol and heptane. In all cases, these domains reproduce the ($\sqrt{3}\times\sqrt{3}$)R30º overlayer structure that is observed in the absence of solvent, and some of them display also the characteristic $c(4\times2)$ superlattice.[1d-f] However, *in situ* vibrational spectra of these monolayers indicate the presence of some conformational disorder near the alkyl chain terminus.[2] There is also a conspicuous lack of reported diffraction results that support the persistence of crystalline order when the monolayer is in contact with a liquid phase. In this communication we report on the time evolution of the diffraction peaks associated with the appearance of the ($\sqrt{3}\times\sqrt{3}$)R30º structure in a 1-nonanethiol SAM deposited on Au(111) from an ethanolic thiol solution.[3] The presence of the liquid phase is shown to disrupt the monolayer structure, and crystallographic order is seen to develop slowly (k ~ $10^{-5}$ $s^{-1}$) only when the contacting solution is removed.

References:

1.- a) J. Pan et al., *Langmuir* **1993**, *9*, 1556; b) R. Yamada et al., *Langmuir* **1998**, *14*, 855; c) G. Nelles et al., *Langmuir* **1998**, *14*, 808; d) F. T. Arce et al., *Electrochim. Acta* **1998**, *44*, 1053; e) M. E. Vela et al., *J. Phys. Chem. B* **2000**, *104*, 11878; f) E. Paradis et al. *J. Electroanal. Chem.* **2003**, *550*, 175.

2.- a) S. M. Stole et al. *Langmuir* **1990**, *6*, 1199; b) T. H. Ong et al., *J. Am. Chem. Soc.* **1992**, *114*, 6243; c) M. R. Anderson et al., *Langmuir* **1994**, *10*, 1638; d) M. R. Anderson et al., *Langmuir* **1996**, *12*, 2327.

3.- M. J. Capitan et al., *Angew. Chem. Int. Ed.* **2006**, *45*, 6166.

# Direct electron transfer kinetics in horseradish peroxidase electrocatalysis

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Direct (mediatorless) electron transfer between several electrode surfaces and more than forty redox enzymes has been observed already, paving the way for the development of "third generation" biosensors.[1] Beyond its elegant simplicity, analysis of the current generated in direct electron transfer experiments can be exploited, under either nonturnover and catalytic conditions, to gain further insight into the mechanisms of electron transfer in biological systems.[2] In this communication we present a detailed steady-state analysis of the nonmediated bioelectrocatalytical activity of adsorbed horseradish peroxidase, as a function of substrate concentration, electrode potential and solution pH.[3] Under steady-state conditions, catalytic currents can be modelled as a series connection of enzyme/substrate and enzyme/electrode kinetic events. We show how these two contributions can be decoupled by taking advantage of their distinct dependence on substrate concentration and electrode potential. The absence of observable nonturnover currents, that prevents a direct determination of the number of active enzymes, has been circumvented by adopting the "binary activity" hypothesis, which leads to consistent results and suggests that only a very low number of enzymes remain fully active at the electrode surface. Upon analyzing the potential dependence of the catalytic currents, a value of ~0.5 eV could be assigned to the reorganization energy for HRP Compound II reduction. Moreover, the variations of the reorganization energy and of the electrode/enzyme electronic coupling with solution pH offer some hints on the nature and location of the acid/base groups that interact with the enzyme/electrode electron-transfer pathway.

References:

1.- a) Ferapontova, E. E. et al. In *Electrochemistry of Nucleic Acids and Proteins, Vol. 1*; Palacek, E. et al. Eds.; Elsevier: Amsterdam, 2005; pp. 517-598. b) Wollenberger, U. In *Comprehensive Analytical Chemistry, Vol. XLIV*, Gorton, L. Ed.; Elsevier: Amsterdam, 2005; pp. 65-130.

2.- Léger, C. et al. *Biochemistry* **2003**, *29*, 8653.

3.- Andreu, R. et al. *J. Phys. Chem. B,* available at the website of the journal.

# The Utilization of Carbon Nanotube Based Composite as Amperometric Biosensor Transducer

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Carbon nanotubes (CNTs) are relatively new nanomaterials that display attractive structural, mechanical, and electronic properties, including improved electrochemical activity that is very important for electrochemical and biosensing applications. Their high electrical conductivity allows them to be used as electrode materials while they can be derivatized with functional groups which permit immobilization of biomolecules. CNTs also have a high surface area-to-weight ratio; most of this surface area is, in principle, accessible to both electrochemistry and immobilization of biomolecules. As electrode materials, CNT can facilitate electron-transfer between the electroactive species and electrodes, and provide a new avenue for fabricating chemical sensors or biosensors. These special properties of both single-wall (SW) and multi-wall (MW) CNTs have attracted the interest of many researchers in the field of electrochemical sensors [1-2].

On the other hand, biosensors can be described as small devices based on the combination of a biological component with a physico-chemical transducer. Carbon based electrodes have been widely used for this process due to their low background current, wide potential window, chemical inertness and low cost. As a composite natured carbon electrode, carbon paste electrodes (CPEs) are widely used as the transducers in biosensor systems since their ease at the preparation, modification and renewal steps [3]. In the present work, MWCNT-included CPE was modified with xanthine oxidase that is very important for the purine metabolism in humans. The enzyme contains FAD, molybdenium, iron and labile sulphur moieties where its enzyme activity is caused by complicated interaction of these substances at or near the active site.

Before modification of carbon electrodes with xanthine oxidase enzyme, the most reactive composite was obtained by examining the cyclic voltammetric results of ferricyanide/ferrocynide system. Then the resulted biosensor working parameters were examined and analytical characteristics were found. The system was also applied for detection of xanthine in plasma samples and very promising results were obtained.

References

1. A.Merkoçi et al. TrAC Trends in Analytical Chemistry, Volume 24, Issue 9, October 2005, 826.
2. M. Pumera et. al. Sensors and Actuators B, *Chemical, Volume 113, Issue 2, 27 February 2006*
3. J. Wang et. al. Electrochem. Commun. 3 (2001) 3600.

# The Utilization of Vanadium Doped Zr-PILCs Nanocomposites For Electroanalytical Applications

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Clays are known as aluminum/magnesium silicates having 1:1 or 2:1 layer structures. Among 2:1 clay minerals, smectite type clays are used for wide variety applications in the various fields. Pillared interlayered clays (PILCs), or pillared clays, are two-dimensional zeolite- like materials. They are prepared by exchanging the native cations of the parent clay with partially hydrated polymeric or oligomeric metal cation complexes which, upon heating, undergo dehydration/dehydroxylation resulting in thermally stable pillars composed of metal oxide clusters (1). Pillared clays (PILCs) have high permanent porosity obtained by separating the clay sheets by a molecular prop or pillaring agent. The interlayer and inter-pillar gallery spacing provide high surface areas and pore's voids. The pore structure also depends upon the type of pillaring species in the interlayer. Among the cations used for pillaring, one of the most profusely used up to the present is a polynuclear hydroxy zirconium complex whose structure is $[Zr_4(OH)_{14}\_(H_2O)_{10}]^2$. Zr-pillared materials with gallery heights of 7, 12, and 14 °A depending on the degree of polymerisation of the zirconium species. (2)

Acidity is the key factor for activation of peroxidic reagents. Because of their low radius/charge ratio, vanadium (V) centers are usually strong Lewis acids, which make them suitable for the activation of peroxidic reagents. The active species has been identified in stoichiometric reactions as mononuclear oxoperoxovanadium (V) complexes. Vanadium (IV) complexes can also be used as precursors in these oxidation reactions. In the presence of excess peroxide, they are readily converted to the oxoperoxovanadium(V) complexes .

In this study V doped Zr-PILCs nanocomposites were used as modifiying reagent for carbon paste electrode (CPE). After the optimization of experimental conditions like vanadium amount in nanocomposite structure, nanocomposite amount in CPE and operating potential, the system was characterized for $H_2O_2$ detection. The usage of obtained electrode as a transducer for monitoring the liberated $H_2O_2$ from enzymatic reactions was also investigated by using model enzyme systems.

***References:***

1. M. Safdar Baksh, Eustathios S. Kikkinides, and Ralph T. Yang, . **Ind. Eng. Chem. Res. 31, 2181-2189 (1992),**
2. S. Moreno, R. Sun Kou, R. Molina, and G. Poncelet,. **Journal of Catalysis 182, 174-185 (1999)**

# A Study on the Electrochemical Impedance Spectroscopy and Responds to Dopamine on Poly (Carbazole-co-p-Tolylsulfonyl pyrrole)-modified Carbon fiber microelectrodes

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The electrocopolymerization of carbazole (Cz) with para-tolyl sulfonyl pyrrole (pTsp) was studied in order to improve the properties of carbazole. The anodic current density of the copolymer in the initial feed ratio of $[pTsp]_0/[Cz]_0=200$ which is obtained from cyclic voltammetry (CV) is higher (0.62 $\mu$Acm-$^{2}$) than that of polycarbazole (0.18 $\mu$Acm-$^{2}$). The characterization of copolymer (Cz and pTsp) was obtained by CV, Fourier transform infrared reflectance spectroscopy (FTIR- ATR) and scanning electron microscopy (SEM). Electrochemical impedance spectroscopy (EIS) results of copolymer, P(Cz-co-pTsp), in the initial feed ratio of $[pTsp]_0$ / $[Cz]_0$ = 200 indicated that the modified CFME gave better capacitance behaviors i.e; specific capacitance ($c_{sp}$=0.156 F cm$^{-2}$) and double layer capacitance ($c_{dl}$=1.85x10$^{-2}$ F cm$^{-2}$) than in the initial feed ratio of $[pTsp]_0$ / $[Cz]_0$ = 1 ($c_{sp}$=2.90x10$^{-3}$ F cm$^{-2}$; $c_{dl}$=4.20x10$^{-5}$ F cm$^{-2}$), $[pTsp]_0$ / $[Cz]_0$ = 2 ($c_{sp}$= 3.4x10$^{-3}$ F cm$^{-2}$, $c_{dl}$=4.82x10$^{-4}$ F cm$^{-2}$), $[pTsp]_0$ / $[Cz]_0$ = 5 ($c_{sp}$= 5.01x10$^{-3}$ F cm$^{-2}$, $c_{dl}$=5.37x10$^{-4}$ F cm$^{-2}$), $[pTsp]_0$ / $[Cz]_0$ = 10 ($c_{sp}$= 9.26x10$^{-3}$ F cm$^{-2}$, $c_{dl}$=1.85x10$^{-4}$ F cm$^{-2}$), Polycarbazole P(Cz) in 0.1 M $LiClO_4$ / ACN ($c_{sp}$= 6.80x10-2 F cm$^{-2}$, $c_{dl}$=1.6x10-2 F cm$^{-2}$), and uncoated carbon fiber microelectrode (CFME) in 0.1 M $NaClO_4$ / ACN. ($c_{sp}$= 5.02x10-3 F cm$^{-2}$, $c_{dl}$=3.97x10$^{-4}$ F cm$^{-2}$). The bode phase angle also approaches a plateau (81$^{o}$) for P(Cz-co-pTsp) in the initial feed ratios of $[pTsp]_0$ / $[Cz]_0$ = 1. The adsorption characteristics of dopamine on the surface of CFMEs were also reported by dopamine concentration with anodic current density (at the maximum peak). A carbon fiber microelectrode modified with electropolymerized films of P(Cz-co-pTsp) in pH 7.0 phosphate buffer solution (PBS) by CV showed an excellent response to the oxidation of dopamine (DA). The detection limit obtained by CV was 1.0x10$^{-6}$ M. The proposed method showed good sensitivity, reproducibility, and stability for the determination of DA. Copolymer has preserved more capacitive and better sensor behavior than polycarbazole and uncoated carbon fiber microelectrodes. The stability of the copolymer coated CFME was tested against dopamine for twenty six days. Although the reversibility is possible only at high scan rates, reversible response can be obtained even at slow rates for copolymer. The ideal reversibility was obtained at 500 mV s$^{-1}$ ($I_a/I_c$=1). Our purpose in this study is to investigate the impedance spectroscopy response of P(Cz-co-pTsp) and to differentiate between capacitive and sensor behaviors. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) methods were studied to characterize the thermal behaviour of PCz and copolymer

# The Electrochemical Behavior of Poly (N-vinyl carbazole) formed on Carbon fiber microelectrodes:

## Responds to Dopamine

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N-vinyl carbazole (NVCz) random polymers were electrochemically coated onto micron-size carbon fibers in tetraethyl ammonium perchlorate / dichloro methane (TEAP / $CH_2Cl_2$) and sodium perchlorate ($NaClO_4$ / ACN) solutions in order to form dopamine-sensing layers on the carbon fiber microelectrodes (CFMEs). The resulting micron-thick polymer films were characterized using scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared reflectance spectroscopy (FTIR-ATR). The responds of microelectrodes to dopamine was investigated using three different electrochemical techniques, cyclic voltammetry (CV), chronoamperometric and chronopotentiometric polarizations, in solutions of tetra ethyl ammonium tetrafluoroborate ($TEABF_4$), sodium perchlorate and lithium perchlorate ($LiClO_4$) in acetonitrile (ACN). The results indicate that at the optimum experimental conditions the electrode shows a reversible and stable behaviour during twenty four days in $TEABF_4$ / ACN solution and, hence, can be considered as a promising sensor for dopamine detection. Sensors displaying a good response to different dopamine concentrations with detection limit of 0.01 nM (3S/N) by CV and chronoamperometry and 1 μM (3S/N) by chronopotentiometry in 0.1 M $NaClO_4$ / ACN. However, detection limits of Poly(N-vinyl carbazole) (P(NVCz)) were obtained as 10 nM (3S/N) by chronoamperometry, 1 nM (3S/N) by CV, and 0.01 nM (3S/N) by chronopotentiometry in 0.1 M $LiClO_4$ / ACN solution. Detection limits of P(NVCz) were obtained as 10 nM (3S/N) by CV, and chronoamperometry, and 0.01 nM (3S/N) by chronopotentiometric methods (Figure 1a, b, and c). The influence of the presence of ascorbic acid on the dopamine signal was analyzed by differential pulse voltammetry (DPV).

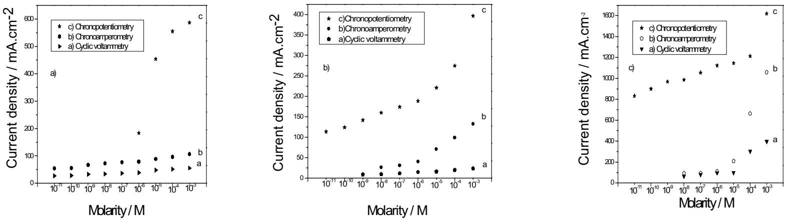

Figure 1. Modified P(NVCz) responds to different dopamine concentrations for the electrode prepared by three different methods (CV, Chronoamperometry, and chronopotentiometry), under different conditions in a) 0.1 M $NaClO_4$/ACN, b) 0.1 M $LiClO_4$/ACN, and c) ) 0.1 M $TEABF_4$/ACN.

# Three – phase electrochemistry with an oil droplet punctured by a cylindrical microelectrode

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Examination of ion transfer across the phase boundary of two immiscible liquids can be approached in several ways. Electrochemistry has become a significant way in this examination. The traditional experimental setup involves 4 electrodes (two reference and two counter), is limited in applications by a relatively narrow potential window and can be applied to well polarizable phase boundaries only. A new recently developed approach has strengthened the electrochemical approach by substantially relaxing the above limitations. The four-electrode setup has been replaced with the three-phase electrochemistry configuration in which an organic liquid drop with a dissolved hydrophobic electroactive compound and without supporting electrolyte is placed on the surface of a graphite electrode and immersed in appropriately composed aqueous solution [1]. The transfer of ions across the phase boundary is triggered by the electrooxidation (or electroreduction) of the compound dissolved in the drop of the organic liquid.

Our first suggestion for further improvement of the electrochemical setup was to use a cylindrical microelectrode that is immersed vertically into a system of two immiscible liquids [2]. Then we came with an idea of a nitrobenzene drop of well-controlled size [3]. The drop is dispensed from a capillary and is punctured with a microcylider electrode. The application of a microcylindrical electrode allows the use of a small-volume voltammetric cell. The employed configuration ensures the stability of the three-phase boundary size and the reproducibility of the electrochemical signals. Also, the examination is not limited to just graphite as the support for the organic liquid drop. The developed approach allows the formation of one or more three – phase boundaries within one small drop. Since the drop is well exposed, this electrode geometry also gives a potential possibility of optical inspection of the reaction products in the organic phase and of examination of the reaction – layer growth.

In this paper we characterize the voltammetric systems with a hanging oil drop. We present the dependence of voltammetric signals on temperature in the presence of various anions in the aqueous phase. This dependence may be very strong. Also, we demonstrate the conditions under which very regular oscillations appear in the measured current. These oscillations are strongly dependent on hydrophilic properties of the anions.

1. Scholz, F.; Komorsky-Lovri , Š.; Lovri , M. *Electrochem. Commun.* 2000, **2**, 112.
2. Bak, E.; Donten, M.; Stojek, Z. *Electrochem. Commun.* 2005, **7**, 483.
3. Bak, E.; Donten, M.; Stojek, Z.; Scholz, F. *Electrochem. Commun.* 2007, **9**, 386.

# Nanostructured poly(methacrylate-aniline) hydrogel as immobilization matrix for electrochemical DNA biosensor

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Electrochemical DNA biosensors are becoming a cheaper, faster and point of care analytical tool for DNA related analysis. But there still exists the challenge of DNA immobilization layers for better electron mediating/molecular wiring, sensitivity, biocompatibility and reusability. The used of dendrimers and hydrogel nanotubes may prove to be advantageous in improving the efficiency and sensitivity of the immobilisation layers. The dendrimers were coated onto the glassy carbon electrode surface by drop coating method before electrochemical interrogation. Poly(methacrylate-aniline) hydrogel (PMAH) mixture containing 2-hydroxyethyl methacrylate (HEMA), aniline/polyanilne (PANI), and other constituent, was spin coated, polymerized using UV irradiation and cured on glassy carbon electrode surface. Nanostructure–favoured synthetic routes for PANI: chemical and electrochemical polymerization, pre-treatment of aniline monomer using interfacial and template free methods were modified and used to semi interpenetrate the PANI into the methacrylate hydrogel matrix. DNA, in a degassed phosphate buffer solution at pH 7 was potentiostatically immobilized on the PMAH and dendrimer modified electrodes and these biosensors were characterized using cyclic voltammetry, electrochemical impedance spectroscopy, UV spectroscopy and scanning electron microscope. The results showed that nanostructured PMAH composites were effective electron transfer mediator for quantitative measurement of DNA hybridization processes.

Keywords: HNCE, nanostructured polyaniline, DNA biosensor, cyclic voltammetry, electrochemical impedance spectroscopy

# Synthesis and Characterization of Alloy vs. Core-Shell Catalysts and Abnormal Diffraction Effects

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Nano-sized Pt based catalysts have attracted much attention due to their potential use as catalysts for the $CH_3OH$ oxidation and $O_2$ reduction for low temperature fuel cells. A second metal is often added to introduce a bi-functional catalytic effect and/or change the electronic state of the platinum. Much work is still needed to improve the Pt based catalysts and to lower the Pt loading in real fuel cell operations. For example, a lowering of four times of the Pt loading of the cathode is needed to bring $H_2/O_2$ fuel cells closer to be used for transportation purposes.

Alloying and/or forming core-shell Pt based catalysts with the metals of the iron group appears a feasible way of improving the catalyst performance and/or reduce the amount of Pt catalysts. This approach has been used in particular for the $O_2$ reduction reaction (orr), where the alloying of Co or Ni with Pt has been shown to lower the over-potential for the orr [1,2]. In this work, the synthesis of core-shell and alloy Pt based catalysts is discussed using chemical reduction methods. Simultaneous and consecutive reduction reactions are utilized to form catalysts that can be subsequently deposited onto suitable substrates. Emphasis is placed on the characterization of the catalysts in order to establish alloy vs. core-shell structure. This is particularly challenging for small catalysts for which methods such as X-ray diffraction are more cumbersome. The latter is partly due to the broadened nature of the diffraction peaks as well as the introduction of unexpected diffraction effects. The X-ray amplitude interference effects that shift the 2-θ angle with maximum intensity for the Pt (111) peak is in a sense opposite to that expected from intensity overlap of peaks (111) and (200), and becomes significant for particles of less than 5 nm in diameter. A reported approach to this problem [3] allows accurate extraction of both crystallite size and content of alloying element from powder profiles of the overlapping (111)-(200) diffraction lines. The method is valid to the cubic close-packed (ccp) solid solutions obeying Vegards's law in the range 0 x 0.6 and will be applied to characterization of the Pt-based catalysts. In addition, the characterization of the prepared catalysts will be discussed using a variety of techniques including the surface characterization by infrared (IR) spectroscopy of adsorbed CO, as well as their electro-catalytic activities and stabilities.

[1] U.A. Paulus, A. Wokaun, G.G. Scherer, T.J. Schmidt, V. Stamenkovic, V. Radmilovic, N.M. Markovic, P.N. Ross, J. Phys. Chem. B, 106 (2002) 4181.

[2] V. Stamenkovi , T.J. Schmidt, P.N. Ross, N.M. Markovi , J. Electroanal. Chem. 554-555 (2003) 191.

[3] Y. Le Page, E. Baranova, C. Bock, P. Mercier, B. MacDougall, Nanotechnology, (2006) (submitted).

# Synthesis, Characterisation and Electrocatalytic Properties of Pt Nanoparticles

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Metal nanoparticles are widely used as electrocatalysts in fuel cell electrodes but the influence of particle size on electrochemical reactivity is still not fully understood. A method for the modification of HOPG with aminophenyl groups for preparing a robust and stable support for Pt nanoparticles prepared in situ is demonstrated. The coverage of HOPG with amino benzene groups was assessed by chemical reaction with cathecol followed by electrochemical determination of the coverage by the quinone using square wave voltammetry (SWV). Platinum nanoparticles were prepared chemically by the adsorption of K2PtCl4 on the NH2-modified electrodes and followed by reduction with NaBH4. This resulted in the anchoring of the catalyst on the electrode surface and allowed further growth. The surface was characterised by XRD and XPS. The dependence of the electro-oxidation of methanol and CO in acid solution at room temperature on particle size was studied for three different sizes of Pt nanoparticles, 2.0, 2.7 and 4.0 nm. It is demonstrated that reactivity for these reactions decreases with decreasing particle size.

# Biosensor Failure Detection Via Neural Network Methodology

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Artificial neural networks (ANNs), proposed by information and neural science as a result of the mechanisms and structures of the brain, are computer programs and they do not attempt to copy the fine detail of how the brain works, but try to reproduce its logical operation using a collection of neuron-like entities to perform processing. ANN can learn the system performance characteristics by monitoring the system test or running data. This technique has grown rapidly in chemistry and related fields of research since 1980's. Until now, ANN is considered as one of the best approaches to the nonlinear calibration and fitting problem.

In current study, glucose oxidase enzyme (GOD) which is specific for the glucose determination was entrapped into polypyrrole matrix containing p-benzoquinone in PIPES buffer and glucose sensitivity of the biosensor is investigated. A calibration curve is plotted for the enzyme electrode as a function of glucose concentration. Because the only useful part of the curve is the linear zone, which is only a small part of the calibration plot, only glucose concentrations in the narrow range can be determined. Whereas, accurate calibration may be reached on this real system by applying ANNs methodology. This implementation can be used for the sensor failure detection in a wide sense. Failure or normal condition of the sensor can be monitored through the difference between actual sensor output and its estimated value. Moreover, the estimation power of the neural network used in the direct and inverse modeling is examined by statistical methods. It presents the good performance for the estimation power.

References:

1- I.Becerik, Ann. Chim.,88, 697, 1998.
2- I.Becerik, S.Seker, Electroanal., 16,18, 1542, 2004.
3- S.Seker, I.Becerik, Ann.Chim., 93, 551, 2003.
4- I.Becerik, S.Seker, Bull. Electrochem., 20, 7, 319, 2004.
5- R. Beale, T.Jackson, Neural Computing:An Introduction, Adam Higler,-IOP Publishing, 161-163., 1991.
6- K.Levenberg, Quarterly Appl.Math. 2, 164-168, 1974.
7- C.C.Liu, J.P.Weaver, A.K.Chen, Electrochim.Acta,8, 379, 1981.
8- M.Gerard, A.Chaubey, B.D.Malhotra, Biosensors-Bioelectronics, 17, 345, 2002.

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

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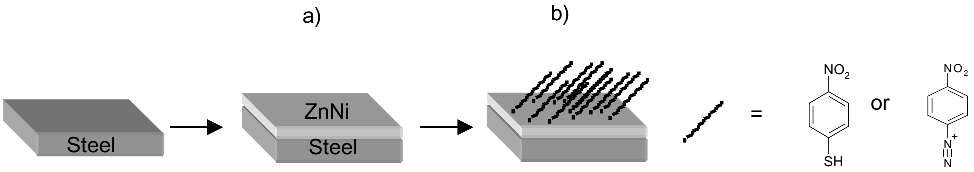
Sacrificial electrodeposited ZnNi is currently studied for replacing chromate conversion coatings (CCC) in anticorrosion applications. The present-day performances of ZnNi are still away from those of CCCs [1,2] and the additional organic layers cannot prevent the corrosive species to reach a metal surface 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] Gavrila, 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-Ul, C. *Chemistry of materials* **2005**, 14, 392-400.

# The Study of Influence of Counter Anion Type on Polymeric Film Morphology

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The influence of the supporting electrolyte on the morphological properties of poly(o-metoxyaniline) (POMA) films has been investigated. The POMA films were synthesized electrochemically on the polycrystalline platinum disks under cyclic voltammetric conditions in aqueous solutions of HCl, $H_2SO_4$ and $HClO_4$, at room temperature. The morphology and thickness of electrosynthesized films were characterized by Atomic Force Microscopy in tapping mode (TM-AFM). It was found that film thickness and morphology strongly depends on the type of counter anion.

It was observed that the dimensions of polymeric structures in dependence on type of counter anion decrease in the order $ClO_4^{-} > Cl^{-} > SO_4^{2-}$.
In $H_2SO_4$ and HCl solutions, at monomer concentration 0.01 M the observed polymer structure is in the form of islands. The surface of electrode itself seems to be still visible. The diameter of structures obtained in $H_2SO_4$ solution was larger, but their number was smaller than those obtained in HCl solution. The shape of the POMA deposits obtained in $HClO_4$ solution was the most regular. For monomer concentration 0.03 M structures obtained in $H_2SO_4$ solution were smaller than those obtained in HCl solution, but their height was twice as big. For polymer film obtained in $HClO_4$ solution the two types of structures were distinguished: trapezium like and spherical (like for in HCl and $H_2SO_4$ solutions). For monomer concentration 0.06 M in $H_2SO_4$ solution fluffy spherical structures have been observed. The chain like structures were obtained in HCl solution. The crystalline like structures were monitored in $HClO_4$ solution.

Thickness of polymeric films in dependence on anion and monomer concentration is presented in the Table.

| Monomer conc. M | $H_2SO_4$ | HCl | $HClO_4$ |
|---|---|---|---|
| 0.01 | islands | islands | 10 nm |
| 0.03 | 110 nm | 250 nm | 340 nm |
| 0.06 | 400 nm | 850 nm | >2000 nm |

# Oxide and hydroxide nanostructures embedded into Anodic Alumina Membranes prepared by means of electrogeneration of base

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Template-directed synthesis utilizing anodic alumina membrane (AAM) has become a popular method to fabricate nanometric-size materials of different nature and for different applications (from catalysis to magnetic memories). In this work we report preliminary results showing the possibility to use an electrochemical route for the synthesis of oxide and hydroxide nanowires and nanotubes with diameters up to 200 nm. The nanostructures were grown into the pores of AAMs through a mechanism called "electrogeneration of base", based on the cathodic reduction of nitrate ions [1].

Both commercial and home-made porous anodic alumina membranes containing nanochannel arrays were used as templates. The morphological structure and the elemental composition of the electrodeposited nanostructured compounds were investigated by scanning electron microscope (SEM) and EDX equipment, respectively, whilst the identification of electrodeposits was carried out by X-ray Diffractometry (XRD).

**The results obtained show that the use of anodic alumina membrane as a template for the direct synthesis of hydroxides and oxides allows to get ordered, crystalline, dense, continuous arrays of high quality nanowires with high aspect ratio.**

## References

1. G. Helen Annal Therese and P. Vishnu Kamath, *Chem. Mater.* 11 (1999) 3561.

# Modification of gold electrodes with metal ion phthalocyanines for the detection of biological thiols

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Transition metallo phthalocyanines have lately attracted a wide research interest. Apart from their use in optical data storage devices and gas sensors, they are nowadays being studied as potential electrocatalysts in the modification of electrodes. The major characteristics of these aromatic compounds are their high thermal and chemical stability, coupled with extensive redox chemistry. The objective of the modification is to provide the electrode with the desired electrochemical properties.

This paper describes the modification and electrochemical behaviour of metal ion phthalocyanines, more specifically copper and cobalt tetra-sulphonated phthalocyanines (CuTSPc and CoTSPc), at a bare gold electrode. The aim is to prepare sensitive electrodes for the detection of biological thiols, such as cysteïne derivatives. These target molecules play an important role in the redox chemistry of living cells and tissues, for example in peptide cross linking, vessel integrity and anti-oxidizing reactions.

The modification was performed using cyclic voltammetry. The latter technique allows the in situ monitoring and control of the adsorption procedure and results in well organized layers of deposition, which is an advantage compared to other commonly used adsorption techniques, such as drop drying and spin coating. The peaks in the voltammogram were assigned to redox reactions on the surface and in the solution. In addition the modification was optimized by investigating the influence of the metal ion phthalocyanine concentration, scan rate and number of cyclic voltammograms on the coverage of the layer. The latter was evaluated using XPS, synchrotron radiation micro-XRF and cyclic voltammetry.

Following the modification, the stability of the modified gold electrodes were evaluated both in the solvent of the deposition as in the medium of the target analytes.

[1] Postdoctoral fellow the Research Foundation Flanders (Belgium)

# Characterization of Carbon Nanotube Modified Screen-Printed Electrodes

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Carbon nanotubes (CNTs) are very interesting nanomaterials for the electroanalytical research area due to their unique electronic, chemical and mechanical properties. A great number of works have been reported in the last three years showing the ability of CNTs to accelerate electron transfer reactions due to their electrocatalytic properties. The most of these works have been developed by modification of conventional carbon paste electrodes or glassy carbon electrodes. However, in this work carbon screen printed electrodes are used to study the theorical favourable electrochemical properties of CNTs.

Single-wall carbon nanotubes (SWCNT), multi-wall carbon nanotubes (MWCNT) and functionalised multi-wall carbon nanotubes (MWCNT-COOH) provided by Fundación Inasmet are used during this work and commercially available carbon screen-printed electrodes are purchased from DropSens (SPEs ref.110).

Dispersion of CNTs is evaluated in several solvents like Triton X-100, SDS, Nafion, ethanol, dimethylformamide or dimethylsulfoxide and some of these solutions were used to characterize CNTs by TEM. Bare SPEs are electrochemically characterised and some SEM images of its carbonaceous microstructure are also presented.

Homogeneous solutions of CNTs are used to modify the surface of the carbon screen printed electrodes and their electrochemical performance is evaluated toward some benchmark redox systems like ferrycianyde, hydroquinone, cathecol neurotransmitters or NADH. These studies demonstrate that CNTs modified SPEs enhance the reversibility of electrochemical processes with rates of electron transfer much faster than those observed for bare SPEs.

The stability of the CNT-SPEs is also tested and their use as electrochemical detectors in a flow injection analysis (FIA) system is proposed. Some scanning electron microscope images of the CNT-SPEs are shown and the electrochemical behaviour is correlated with the nanoscopic structure of the modified electrodes.

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# Impedimetric genosensing using gold-streptavidin nanoparticles for signal amplification

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Electrochemical Impedance Spectroscopy is an electrochemical technique which is rapidly developing as a tool for studying DNA hybridization [1]. The technique is an effective method to probe the interfacial properties (capacitance, electron transfer resistance) of modified electrodes. Many different protocols have been recently used in DNA detection by this technique. Some of them employ different types of nanoparticles as a way to increase the sensitivity of the method [2].

In this work, gold nanoparticles coated with streptavidin are used for the amplification of DNA hybridisation detection by Electrochemical Impedance Spectroscopy. The used protocol is as follows.

A graphite epoxy composite transductor (GEC) was used as working electrode. The probe oligomer was adsorbed onto the electrode surface and the impedance measurement was performed in a solution containing the redox marker ferrocyanide/ferrycianide [3]. A biotinilated complementary oligomer (target) was then added, its hybridization was allowed and the measurement performed in the same way as above. The change of interfacial electron transfer resistance ($R_{et}$) between the solution and the electrode surface, due to the reaction of the redox marker at the applied potential, was recorded to confirm the hybrid formation. When target oligomer hybridized with the probe, the double helix film formed on the electrode led to a strong increase of the interfacial electron transfer resistance value ($R_{et}$), which constitutes the useful analytical signal.

The same electrodes were then incubated in a solution containing gold streptavidin nanoparticles. Streptavidin modified nanoparticles bound to biotinilated target oligomer thanks to the strong streptavidin-biotin interaction. This additional surface modification led to a further increment of $R_{et}$ thus obtaining significant signal amplification.

To confirm the performed stages, gold nanoparticles on the electrode surface were observed by Scanning Electron Microscopy (SEM) after a Silver Enhancement treatment. This last step produced an additional $R_{et}$ increment in the recorded impedance spectra.

**References:**

[1] E. Katz, I. Willner, Electroanal 15 (2003) 927
[2] Y. Xu, H. Cai, , P.G. He, Y.Z. Fang, Electroanal 16 (2004) 150
[3] A. Bonanni, M.J. Esplandiu, M.I. Pividori, S. Alegret, M. del Valle, Anal. Bioanal.Chem, 385 (2006) 1195

# Photoelectrochemical Characteristics of CdTe Quantum Dot Modified Electrodes

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Semiconductor nanoparticles are promising candidates as photoactive materials in electroluminescent and photovoltaic devices [1]. This work presents the results of photoelectrochemical invtestigations on alternating multilayer systems composed of 3-mercaptopropionic acid (MPA) protected CdTe quantum dots (q-dots) and the polycation Poly(diallyldimethylammonium chloride) (PDADMAC) on ITO.

Aqueous colloids of the ligand protected CdTe q-dots were prepared following a two-step synthesis protocol [2]. By sequential electrostatic adsorption of the q-dots and the PDADMAC on ITO, electrodes with different number of layers were fabricated. Photocurrent responses were recorded in the presence of hole-scavenging sulphite ions (0.1 M $Na_2SO_3$). This configuration yielded anodic photocurrents with a very strong potential dependence and low quantum efficiencies ($\eta < 0.05$ %). The origin of the potential dependence of the photocurrent is rationalised in terms of the position of the q-dot band edges [3] and the Fermi level at the ITO electrode. Logarithmic increase in the photocurrent with the number of $(PDADMAC/CdTe)_n$ layers reveals the less efficient electron transfer from the outer layers to the electrode.

References

1.- P. Weiss, Science News, **169** (2006) 344

2.- H. Zhang and B. Yang, *Thin Solid Films*, **418** (2002) 169

3.- G. Kissling, Ch. Bünzli and D.J. Fermín, poster presentation, ISE Spring meeting, Dublin, 2007.

# Good’s Buffers Inert or not? An Electrochemical Study.

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Good’s Buffers, such as HEPES (2-[4-(2hydroxyethyl)piperazinyl]ethanesulfonic acid) and TRIS (tris(hydroxymethyl)methylamine) are popular pH buffers, which are extensively used in laboratories of analytical, inorganic, physical chemistry, biological, biochemical and also in tissue culture. This is because of their convenient pKa value (HEPES = 7.55, Tris = 8.1), high solubility, and minimal tendency to form complexes with metal ions. Recent studies, however, indicate that HEPES and Tris are not so inert as previously believed. To verify this we performed an electrochemical study on HEPES and TRIS.

In this study the voltammetric activity of HEPES and Tris has been investigated. The buffer solutions show a redox process when in contact with oxygen, which remains visible when the same solution is brought under anaerobic conditions. When the buffer solution, on the other hand, was measured directly under anaerobic conditions, the redox process was not observed (Figure). A possible explanation for these phenomena is the formation of radicals in contact with oxygen. To confirm this a comparison between HEPES, TRIS and a phosphate buffer were made.

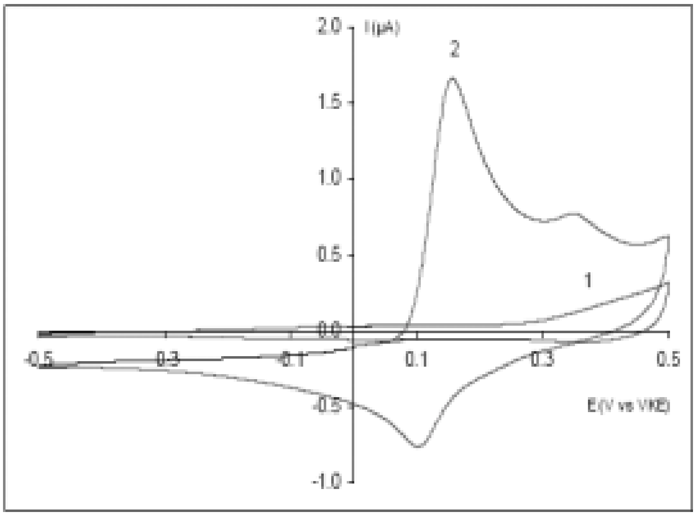

*Figure: Cyclic voltammograms of a gold electrode measured in a 10 mmol $L^{-1}$ Tris buffer solution. Curve 1 is measured in the absence of oxygen, curve 2 is measured in the absence of oxygen after a measurement in oxygen atmosphere. Start potential = 0 V vs SCE, first vertex potental = 0.5 V vs SCE, second vertex potential = -0.5 V vs SCE and polarisation rate = 10 mV $s^{-1}$.*

# Electrochemical detection of hydrogen peroxide with *Rhodobacter capsulatus* cytochrome *c* peroxidase at a gold electrode

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Spontaneous or electrochemical adsorption of proteins onto electrodes is the most recent development in the research field of bio electrochemistry. It is self-evident that the maintenance of the original properties of the proteins is a major goal, implying that denaturation should not occur. The interactions between a protein and the electrode can be weak or strong; weak interactions give rise to diffusion controlled processes of the species in the solution, while with strong interactions the protein film acts as a monolayer. The electrical contact between the bio catalyst and the electrode is important for the development of biosensors and bio electronic devices.

Voltammetric analysis of the electrode modified with enzymes is an interesting tool for the study of oxidation and reduction reactions of redox enzymes. The activity of the enzyme can be determined by measuring the current corresponding to the target molecule. An electrochemical study of the redox process can lead to important information concerning the kinetics of the reaction.

As protein system, *Rhodobacter capsulatus* cytochrome *c* peroxidase (CCP) was selected. The aim is to immobilize the enzyme onto a gold electrode. Different linkers, acting as a mediator between the electrode surface and the enzyme, were tested: 4,4'-bipyridyl, mercapto hexanol and mercapto propionic acid. The research also showed that CCP can form a complex with Horse Heart cytochrome c (HHC). This complex is a perfect mediator for the electrocatalytic reduction and thus the detection of hydrogen peroxide.

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# Electrochemical Studies of Single-Stranded DNA Self-Assembled Monolayers on Gold Electrode Surfaces

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We present electrochemical studies of the immobilization of single-stranded DNA (ssDNA) on gold electrode surfaces. The effect of immobilization time on surface coverage was probed by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). Additionally, linear sweep voltammetry was used to perform reductive electrochemical desorption of the ssDNA molecules, and the variations in surface coverage. Charge transfer resistance ($R_{ct}$) and capacitance with desorption cycles were monitored by EIS. The results show surface coverages greater than 0.9 for immobilization times of 15 hours or more (see Figure 1). The coverage and $R_{ct}$ increased, while the capacitance decreased for higher immobilization times. The opposite trend was observed for an increasing number of desorption cycles. These results suggest that a combination of variations in immobilization time and number of desorption cycles represents an alternative to optimize the density of immobilized ss-DNA, which is desirable for the subsequent optimization of DNA hybridization and the development of DNA biosensors. Similar studies have been made by switching the potential of ssDNA molecules modified Au electrodes. The capacitance at the two switching potentials is indicative of a possible detection method for the hybridization process. This has been coupled with fluorescence probes for the structure determination of the ssDNA modified Au surface.

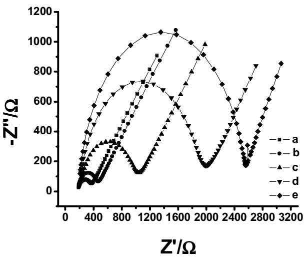

Figure 1: Nyquist plot (in 5mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 0.1 M KCl; The figure shows how the Nyquist plot for bare Au (a) change after modification with disulfide-modified DNA during 0.25 hour (b), 1 hour (c), 15 hours (d) and 48 hours (e).

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# Selective permeation of a liquid-like SAM of 11-amino-1-undecanethiol (AUT) on polycrystalline Au by redox probes

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The compact full-coverage structures of SAMs formed by long chain alkanethiols on Au strongly block the electron transfer (ET) of electroactive species in solution[1]. Nevertheless, this behavior has been contradicted for substituted thiols with different terminal charged endgroups [2, 3] whose redox response showed to be governed by electrostatic interactions established at the SAM-solution interface between such endgroups and the probes. It created some controversy and many authors still associate this behaviour to the formation of very defective or low coverage films.

CV and Electrochemical Impedance Spectroscopy (EIS) experiments were performed for an Au polycrystalline rod electrode, previously immersed in an AUT 1 mM solution in ethanol, in $NaClO_4$ 0.3 M showing a large increase in the capacitor behaviour which contradicts the formation of highly defective films. The modified electrode was also checked in the presence of 2 mM $[Ru(NH_3)_6]^{+3}$ and $[Fe(CN)_6]^{-3}$ in KCl 0.2 M. At short immersion times, after the first SAM-solution contact, a strong blockage of the electron transfer was obtained in the first case while the redox activity resembled the one for the bare Au electrode in the presence of hexacyanoferrate. For longer contact times the ET processes became increasingly facilitated and hindered respectively. Electrochemical characterization of the modified electrodes in $NaClO_4$ 0.3 M, after more than 24 hours immersion in the probe solutions, showed a negligible thiol desorption.

The results obtained strongly agree with a model of selective permeation of the AUT layer controlled by the nature of the electrostatic interactions. It has been shown in the literature that the inclusion of charged or bulky terminal endgroups can introduce distortion from the archetypal structure formed by alkanethiols on Au, by steric constraint or endgroup-endgroup interactions [4, 5]. In addition, the natural phase transitions observed in unsubstituted SAMs (liquid-like structures) could be stimulated and allow the accommodation of solution species into the film. The electrostatic binding of electrolyte anions to the endgroups with progressive neutralization of the surface charge (and, thus, changing the nature of the interactions and the permeation properties of the layer) has been suggested as an explanation for the shift in the ET properties with the contact time although it still needs to be further investigated.

[1] M. D. Porter, D. L. Allara, C. E. D. Chidsey, *J. Am. Chem. Soc.*, 109, 12 (1987), 3559
[2] K. Takehara, H. Takemura, Y. Ide, *Electrochim. Acta*, 39, nº6 (1994), 817
[3] T. H. Degefa, P. Schön, D. Bongard, L. Walder, *J. Electroanal. Chem.* 574 (2004),490
[4] H. –J. Himmel O. Dannenberger, M. Grunze, C. Wöll, *Langmuir* 13 (1997), 4943
[5] Dannenberg, H. –J. Himmel, M. Buck, C. Wöll, *Thin Solid Films* 307(1997), 183

# Characteristics of supercapacitor electrodes of Carbon black/PAN carbon nanofiber

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Various materials have been tried for developing supercapacitors. Such as activated carbon(AC), activated carbon fiber(ACF), metal oxides ($RuO_2$, $IrO_2$, and $MnO_2$, etc.), and carbon nanotubes (CNTs), etc. are good candidates for electrodes of supercapacitors. Many researchers look for the materials having both high capacitance and lower cost. Carbon black(CB) is well adapted to allow the electrolyte accessibility because of their high electric conductivity, good mechanical properties, low cost, and so on.

Electrospinning is a good method to fabricate nanofibers using electrostatic force between polymer solution and collector.

We focus on the fabrication of CB/PAN carbon nanofibers via electrospinning and the examination of the potential electrode of supercapacitors. The physical and electrochemical properties of CB/PAN carbon nanofibers were characterized by SEM, BET, CV, and so on.

The 4~20wt% CB/PAN nanofibers of about 205~240 nm diameter were prepared by co-electrospinning. Electric conductivity of 8wt% CB/PAN carbon nanofibers increased to 8.06 mS/cm compare to that of pure PAN carbon nanofibers. But, the specific capacitance of 8wt% CB/PAN decreased to 110 F/g compare to that of pure PAN as surface area decreased.

# Electrochemical properties of supercapacitor electrodes of polyacrylonitrile nanofibers

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Electrospinning is a process that produces continuous polymer fibers with diameter in the sub-micron range through the action of an external electric field imposed on a polymer solution. Polyacrylonitrile (PAN) nanofibers were fabricated by co-electrospinning technique. The fabricated PAN nanofibers were characterized using scanning electron microscopy (SEM).

In this work, we focus on the fabrication of PAN-based nanofibers by electrospinning and the electrochemical properties of electrode of supercapacitors. 7.4~15 wt% PAN nanofibers of about 205~280 nm in diameter were fabricated. The average diameter of PAN nanofibers increased with increasing the concentration of PAN solution, average diameter of nanofibers increased from around 200 nm to 800 nm. It has been found that the concentration of PAN polymer solution strongly affects the size of the fibers so that diameter of fibers increases with increasing the concentration of the solution. Also the applied voltage is strongly correlated with the distribution of nanofibers. In addition, we found an evidence that electrostatic effects influence the stability of discharge.

The electrochemical properties of electrode of supercapactor were characterized by CV, battery cylcer and so on.

# Label-Free DNA-Sensing Using Gan Nanowires Nanosensor

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A novel DNA-sensing system based on GaN nanowires (NWs) is presented coupled with their electrochemical impedance and photoluminescence measurements. GaN, an important III-nitride semiconductor, being a direct and wide band-gap material, were renowned for their potential in optoelectronic application and their inherent bio-compatibility. However, their true application in bio-sensors has been surprisingly absent till date. Simultaneously, one-dimensional (1D) nanostructures have attracted huge interest as potential building blocks for the future nanoelectronic devices. In this report, GaN NWs are used as a transducer for DNA-sensors, by immobilizing ssDNA molecules through covalent binding using organosilane linker (MPTS)*. The immobilization of ssDNA and the subsequent hybridization to dsDNA were confirmed using confocal microscope. Electrochemical impedance measurement showed that interfacial electron-transfer resistance (Ret), from solution to transducer surface, increased significantly when pristine GaN NWs were immobilized with ssDNA, along with a formation of additional semicircle region at lower frequency in Nyquist plot. The unique appearance of double-semicircle region for ssDNA-immobilized NWs, compared to single-semicircle region for pristine GaN NWs, leads to the idea of formation of double-capacitance layer in series. The phenomenon is more prominent by the appearance of double peaks in the plot of phase angle vs. frequency (Bode plot), the second peak, formed after ssDNA-immobilization, showed further increase under the hybridization to dsDNA, and consequently reduces the overall impedance. Moreover, quenching behavior in photoluminescence of the GaN NWs was distinguishable for the ones immobilized with ssDNA and the same hybridized to dsDNA. Both the technique implies the ability of oligonucleotides, immobilized on the NW-surface, to interact with other biomolecules. The dual and label-free sensing capability in impedance and photoluminescence of GaN NWs makes them effective DNA transducers.

# Are We On The Same Wavelength? Tuneable Photonic Crystal Structures As Highly Reproducible SERS Substrates.

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Raman spectroscopy is a non-destructive, non-invasive vibrational spectroscopic technique, however only 1 in $10^{12}$ photons are Raman scattered which make the process very weak. Surface Enhanced Raman Spectroscopy (SERS) was discovered by Fleischmann *et al.*[1] when an electrochemically roughened silver electrode was used to obtain Raman spectra of pyridine. Since this discovery, many different substrates have been developed, however none have shown the reproducibility or robustness required to fulfil the potential of SERS. A nanostructured substrate has been prepared via electrodeposition of metal through a template of polystyrene spheres, producing an opalescent film with many interesting and tuneable optical properties. Surface plasmon modes are the key to understanding the SERS signals achieved. The greatest SERS signal is seen when the ingoing laser wavelength and the outgoing Raman scattered photon overlap with a surface plasmon mode, therefore by varying the void diameter and film thickness the ideal substrate for different excitation laser wavelengths and molecules can be prepared. The development of this sculpted substrate allowed SERS to be achieved reproducibly both *in-situ* and *ex-situ*. However, most importantly, SERS has been obtained from many different metals, including platinum, palladium, gold and silver[2-4] Obtaining SERS from platinum and palladium enabled many important electrochemical reactions to be monitored using *in-situ* SERS. Results will be presented of a study of CO adsorption at both Pt and Pd sculpted electrode surfaces.

1. Fleischmann, M., P.J. Hendra, and A.J. McQuillan, Chem. Phys. Lett., 1974. **26**(2): p. 163-166.
2. Abdelsalam, M.E., et al., J. Am. Chem. Soc, 2007. **Submitted**.
3. Cintra, S., et al., Faraday Discussions, 2005. **132**: p. 191.
4. Cintra, S., et al., Appl. Spectrosc., 2007. **Submitted**.

# Corrosion Inhibition Of Stainless Steel By Using Ketone Based Resins

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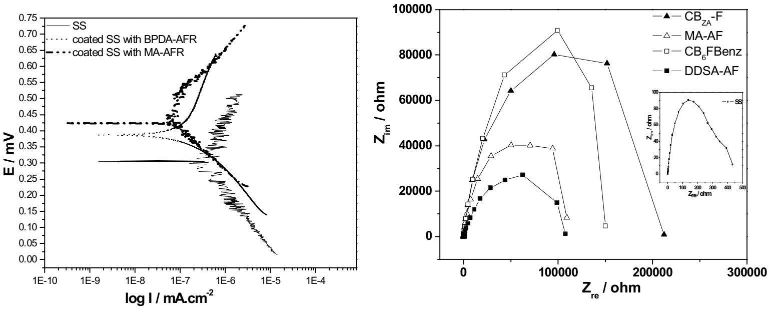
The corrosion of steel has long been an important problem, causing losses in excess of 100 billion dollars annually world wide [1]. Thus, efforts to develop more efficient and environmentally compliant methods to prevent corrosion have been ongoing throughout this century [2]. The use of polymers for the protection of metals against corrosion has been recently investigated [3].
In this study, effect of some newly synthesized modified ketonic resins [4] on corrosion inhibition of stainless steel (SS) was investigated in acidic medium. Carboxyl, hydroxyl and acetyl functionalized resins have been coated on metal electrode as a thin film by dipping method. Corrosion currents were obtained by Tafel extrapolation from anodic and cathodic polarization curves of these films. Impedance measurements were used for characterization and polarization resistance was obtained from these measurements. The stability of polymeric coating were tested with time in acidic medium.



(a) (b)

**Fig 1. (a)** Tafel plots of bare and coated with Acetophenone-Formaldehyde resin modified with Maleic Anhydride (MA-AFR) and Biphenyl tetracarboxylic Dianhydride (BPDA-AFR) **(b)** Nyquist plots for bare and coated with Cyclohexanone-benzaldehyde-formaldehyde (CB$_{ZA}$-F), Maleic Anhydride (MA-AFR), Cyclohexanone-bisphenol-C-formaldehyde (CB$_6$F), Acetophenone-formaldehyde-dodesenilsucsinic-anhydride (DDSA-AF) stainless steel

References:
1. N. Ahmad and A.G. MacDiarmid, Synth. Met. 78 (1996) 103
2. S.P. Sitaram, J.O. Stoffer and T.J. O'Keefe, J. Coat. Technol. **69** (1997), p. 65.
3. S.-Y. Zhang, X.-W. Luo, S.-J. Li, W.-F. Zhou, Huaxue Tongbao (Chemistry) 31 (1997)
4. N. Kızılcan, A. Akar; J. Appl. Polym. Sci. 60, (1996) 465-476.

# Electrical properties of electrochemically deposited single bismuth nanowires

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In recent years, bismuth nanowires were intensively studied both because of their unique electronic properties and possible future application in thermoelectric devices. When the size of an object becomes comparable to the electronic mean free path $l_e$ and Fermi wavelength $\lambda_F$, finite-size and quantum-size effects are expected, respectively [1]. Since these parameters are large in bismuth ($l_e \sim 100$ nm and $l_F \sim 40$ nm at room temperature), such effects are anticipated for wires of comparatively large diameter, making bismuth an ideal material for studies on the nanoscale. Finite-size effects include additional electron scattering from inner grain boundaries and the wire surface.

Single bismuth nanowires are deposited electrochemically in ion track-etched polycarbonate membranes [2]. The crystallinity is controlled by the fabrication conditions, in particular the choice of overpotential and temperature. The wires are contacted while left embedded in the template. The specific electrical resistivity is found to be strongly influenced by the mean grain size $D$ and increases with decreasing $D$. For wires with diameters $d < 150$ nm the resistivity rises with diminishing $d$. In addition, the resistance is a non-monotonic function of temperature. While the carrier mobility for bulk Bi increases by three to four orders of magnitude when cooling down from room temperature to 4 K, it saturates at a few ten Kelvin for nanowires. All observations are attributed to finite-size effects [3]. Further, we studied the maximal current density $j_{max}$ the wires are able to carry. Bulk metals fail because of joule heating at current densities of $10^3$ to $10^4$ A/cm$^2$ [4]. Since for bismuth the specific electrical resistivity is more than fifty times higher than in conventional metals and the melting temperature amounts only to 271°C it is expected that bulk Bi fails at lower $j_{max}$. For wires with diameters below 1 µm we found that $j_{max} > 10^5$ A/cm$^2$ and that it increases with decreasing diameter. Since the surface-to-volume ratio rises with diminishing $d$, the wires may dissipate the heat more easily to the surrounding material involving the rising $j_{max}$.

[1] V.B. Sandormirskii, Sov. Phys. JETP 25 (1967) 101
[2] T.W. Cornelius, J. Brötz, N. Chtanko, D. Dobrev, G. Miehe, R. Neumann, M.E. Toimil-Molares, Nanotechnology 16 (2005) S246
[3] T.W. Cornelius, M.E. Toimil-Molares, R. Neumann, S. Karim, J. Appl. Phys. 100 (2006) 114307
[4] P.S. Ho, T. Kwok, Rep. Prog. Phys. 52 (1989) 301

# A Theoretical Study on the Electronic Coupling between Azurin and Gold at Different Protein/Substrate Orientations

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Azurin is an electron transfer protein (of the cupredoxin family) that has been widely studied to clarify the specific features of biological Electron Transfer (ET) [1]. In more recent years, azurin has been considered as a promising candidate for the implementation of prototypical biomolecular electronic devices [2]. In this context, and more generally to unravel its ET properties, different Scanning Probe Microscopy (SPM) have been performed on the molecule supported on solid electrodes [3-5]. In some of these studies, azurin was immobilized via a solvent exposed disulphide bridge on a gold (111) electrode. Since such a disulphide is located in a protein region far (~2.5 nm) from the redox active site, relatively small orientational variations implies quite large gold-active site distance changes.

Starting from this observation, we have computed, by means of long constrained classical molecular dynamics simulations, the structure of azurin deposited on a Au(111) surface at different possible orientations and the forces needed to constrain the protein at each sampled conformation. Relative gold-protein electron transfer rates for various conformations have been estimated by means of the average packing density [6] and the tunnelling pathways models [7]. We found a strong dependence of the azurin/gold electronic coupling on the molecular orientation. In particular, it is greatly enhanced by forcing the protein to lie as flat as possible on the surface. The implications of our results for scanning probe microscopy experiments are also discussed.

[1] H.B. Gray and J.R. Winkler, *Proc. Natl. Acad. Sci. USA* **102** (2005), p. 3534.
[2] G. Maruccio, A. Biasco, P. Visconti, A. Bramanti, P. P. Pompa, F. Calabi, R. Cingolani, R. Rinaldi, S. Corni, R. Di Felice, E. Molinari, M. P. Verbeet and G. W. Canters, *Adv. Mater.* **17** (2005), p. 816.
[3] (a) E. P. Friis, J. E. T. Andersen, Y. I. Kharkats, A. M. Kutznetsov, R. J. Nichols, J.-D. Zhang and J. Ulstrup, *Proc. Natl. Acad. Sci. USA* **96** (1999), p.1379; (b) Q. Chi, O. Farver and J. Ulstrup, *Proc. Natl. Acad. Sci. USA* **102** (2005), p.16203.
[4] J. J. Davis, C. L. Wrathmel, J. Zhao and J. Fletcher, *J. Mol. Rec.* **17** (2004), p.167.
[5] see also A. Alessandrini, S. Corni and P. Facci, *Phys. Chem. Chem. Phys.* **8** (2006), p.4383 and Refs. therein.
[6] C. P. Page, C. C. Moser, X. Chen and P. L. Dutton, *Nature* **402** (1999), p.47.
[7] J. N. Betts, D. N. Beratan and J. N. Onuchic, *J. Am. Chem. Soc.* **114** (1992), p.4043.

# Spectroscopic and Electrochemical Measurements of Cytochrome C at Gold Surfaces Modified with mixed SAMs.

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The factors controlling the redox potential, E°', of proteins and enzymes are of particular importance to those investigating their biological function. The realisation that proteins can function in non-aqueous solvents has also widened their potential applications in biosensing and biocatalysis and in turn, has generated an interest in the effect of solvent on protein behaviour. It is important therefore to gain an understanding of how protein properties, such as redox potential and electron transfer kinetics, are affected by solvent composition. However, little is known about the structural or conformational changes that enzymes, in particular redox enzymes, undergo in organic solvents.

A range of Au surfaces (Au disk electrodes; Au mesh electrodes and Au deposition on ITO (Au|ITO electrodes) were modified using a mixed $C_{10}/C_7$ self-assembled monolayer (SAM). The resulting electrodes are easy to prepare, stable, robust and suitable for modification. These optically transparent electrodes (OTE's) enable the examinmation of both spectroscopic (UV-Visible spectroscopy (UV-Vis); resonance Raman (rR) and circular dichroism (CD)) and electrochemical processes at their surfaces'. CD can be used to monitor conformational changes in the secondary structure of proteins and is used to monitor the conformational changes that attend oxidation and reduction of cytochrome c in organic solvents. These electrodes are useful for both basic studies of protein/electrode interaction and for the development of analytical biosensor devices utilising combined optical and electrochemical signals.

# Development and electroanalytical properties of composite electrodes modified with $ZrO_2$ nanogels

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The need for new, rapid and sensitive sensors for the analysis of pharmaceutical products has oriented our researches towards the development of composite electrode materials.

Continuing our previous researches [1, 2] we present here the development of a new amperometric biosensor for the detection of paracetamol (acetaminophen) by using two electrodes configuration. The carbon paste electrodes doped with various amount of $ZrO_2$ present lower analytical characteristics (sensitivity, response time and limit of detection) than the film electrodes. The last were prepared by deposition of a thin film of polyethyleneimine doped with different amounts of $ZrO_2$ to give well-defined calibration plots. The developed electrodes present some attractive properties such as simplicity of preparation, mechanical stability, interesting analytical and electrocatalytic properties.

Comparative studies between non-enzymatic and enzymatic electrodes were performed in order to test the permeability of the deposited film and the electrocatalytic activity of nanogels.

The obtained results showed an efficient interaction between the electrode surface, nanogels and the biocomponent.

The presentation will show the details regarding the synthesis and characterization of the used nanogels as well as the electrocatalytic activity of the films deposited onto the glassy carbon electrodes. The development of an original configuration for the paracetamol biosensor will be described.

References:

1. D. Yu, Olga Dominguez Renedo, B. Blankert, Veronica Sima, R. Sandulescu, J. Arcos, J-M. Kauffmann, *Electroanalysis*, 18, 2006, 1637-1642
2. N. Bonciocat , I.O. Marian, R. Sãndulescu, Cecilia Filip and S. Lotrean, *J of Pharma. and Biomed. Analysis*, 32 (4-5), 2003, 1093-1098

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# Nanostructure nickel hydroxide modified electrodes for urea determination

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The urea concentration in serum or urine, is an indicator of kidney diseases, as well diabetes, and analysis in clinical laboratories is very frequent. However, the urea quantification uses conventional methods, such as spectrophotometric with indophenol[1]. In this way, the development of new routes to urea determination is very important, and the sensors are a very good alternative that involves a low cost, fast response, and others qualities. The aim of the present work remains improving amperometric urea determination using nickel hydroxide nanostructured and also electrodeposited. Nanosized nickel hydroxide was synthesized by a sonochemical method, deposited onto ITO transparent electrodes by using the electrostatic deposition layer-by-layer technique with 5 bilayers [2]. Regarding a comparison to the nanostructured nickel hydroxide, bulk films were prepared by electrodeposition from a solution $Ni(NO_3)_2$ 0,05 mol $L^{-1}$ on I.T.O electrodes, applying a current of - 0.1 A $cm^{-2}$ during 7200 s. The electrochemistry behavior of the nickel hydroxide electrode was investigated through a cyclic voltammogram, in NaOH 1.0 M, where was observed two peaks in the profile in 0,410 and 0,280 V, corresponding at redox couple Ni(II)/Ni(III) [2]. A sensor for urea presenting a satisfactory answer can be obtained by immersion of $Ni(OH)_2$ film in a NaOH 1.0 M solution and applying a potential of + 0,435 V, where the maximum one occurs of anodic current in the cyclic voltammogram. Analyzing the results it can be observed that for a range of analite concentration between 5 to 50 mM, the behavior presents linear and the sensibility found was 29,5 and 20,3 mA $cm^{-2}$ $M^{-1}$, for nanosized and bulk films, respectively. These values are greater than those reported for bulk electrodeposited films where the amount of active material is greater, indicating that nanometric size and defined geometry are relevant parameters for enhancing the properties of metal hydroxides for urea determination. Both films present excellent reproducibility for urea determination. Also films contain 5% of cobalt hydroxide were investigated but the sensibility presents less values.

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[1] J. K. Fawcett, J. E. Scott. *J. Clin. Pathol.*, **13** (1960) 156.
[2] **M.** Vidotti, C. van Greco, E. A. Ponzio, S. I. Córdoba de Torresi, *Electrochemistry Communications*, **8** (2006) 554.

# Layer-by-layer films of polyaniline and polysaccharide for biomaterial application

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New tissue engineering technologies will rely on biomaterials that physically support tissue growth and stimulate specific cell functions. The goal of this study was to create a biomaterial that combines inherent biological properties which can specifically trigger desired cellular responses (e.g., angiogenesis) with electrical properties which have been shown to improve the regeneration of several tissues including bone and nerve [1]. With this aim, composites of the biologically active polysaccharide botryosphaeran (EPS) secreted by the ascomyceteous fungus *Botryosphaeria rhodina* and the electrically conducting polymer polyaniline (PANI, polyemeraldine base) was synthesized and characterized.

Layer-by-layer films of PANI/EPS were obtained using HCl pH 2.0. It was utilized solution of polyemeraldine base in concentration of 0.21 mg/mL and solution of the polysaccharide botryospheran in concentration of 0.45 mg/mL. The pH of the solutions was corrected to 2.0 with HCl concentrated. The deposit of 30 bilayers in ITO surface was accompanied by the UV-vis spectroscopy, regarding that the absorbance increased gradually with the addition of the number of layers revealing the uniformity in the deposition. Characteristics bands of the PANI and of the EPS were observed us spectra of FTIR of the film. The 1715 and 1590 $cm^{-1}$ peaks have been attributed to the aromatic C=N bond (quinoid) of the polyemeraldine base. The strong band seen at 1325 $cm^{-1}$ can be assigned to the combination of several stretching and bending vibrations emanating from the C=N bonds. The peak at 875 $cm^{-1}$ can be understood to arise from the C=H stretching of emeraldine base [2]. The electrochemistry behavior for to the PANI/EPS film, in HCl pH 2.0, showed two redox peaks in the cyclic voltammograms, characteristics for the PANI films [2]. The film of PANI/EPS presents an increase in current peaks when compared with the film PANI without the EPS, in the first peak oxidation, and still verifies a displacement for less positive potentials. Such evidences confirm to the interaction of the conducting polymer with the polysaccharide.

*Acknowledgements:* Fundação Araucária, CNPq and CAPES.

[1] Bidez PR, Li SX, MacDiarmid AG, Venancio EC, Wei Y, Lelkes PI, "Polyaniline, An Electroactive Polymer, Supports Adhesion And Proliferation Of Cardiac Myoblasts" *Journal of Biomaterials Science-Polymer Edition* 17 (**1-2**): 199-212, 2006

[2] Ram MK, Salerno M, Adami M, Faraci P, Nicolini C “Physical properties of polyaniline films: Assembled by the layer-by-layer technique“ *Langmuir*, 15 (**4**) 1252-1259, 1999.

# Surface modification of a silicon substrate by Pt nanoparticles and study of the new electrochemical properties

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Electrochemistry plays a major role for the preparation and the characterization of nanometric metal structures. The electrochemical deposit of platinum nanoparticles on a silicon substrate was considered with the aim of obtaining new electric properties on a nanometric scale on the surface of the semiconductor. The new Si/Pt structures offer many possibilities of applications in various fields, in particular in micro-electronics, photovoltaic cells and microsensors.

In this work, we have obtained results with single-crystal silicon substrates (100) of p-type and n-type. The deposits of platinum nanoparticles on the substrates were carried out by cathodic electrodeposition under illumination using a commercial plating solution.

First, we studied the effect of the experimental conditions on the deposit quality. The growth mechanism of the nuclei could be determined by electrochemical methods, whereas the morphology of the Pt nuclei was investigated by atomic force microscopy, the aim being to understand the development of Pt nanoparticles in order to be able, thereafter, to control their nucleation and their growth.

Second, it was necessary to study the electrochemical and physico-chemical properties of these new structures. After having defined the new characteristic parameters, we could study and compare their electrochemical behavior in an electrolytic solution containing a redox couple used as a charge transfer probe.

Thus, we could note that platinum has different effect on the electrochemical properties of the two substrates. In the case of a p-Si electrode, the presence of the platinum particles completely modifies the electrochemical behavior, which approaches that of a platinum electrode. In the case of a n-Si electrode, the presence of Pt raises the potential barrier of the space charge layer, and the blocking of the charges transfer on the anodic side is always observed. On the other hand, under illumination, the effect of Pt on the n-type and p-type substrates is different. Platinum tends to increase the photoelectrochemical properties of n-Si electrode and to decrease those of p-Si electrode.

# Electrochemiluminescent Monolayers on Metal Oxide Electrodes: Detection of Amino Acids

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The importance of amino acid detection continues to grow in both the chemical and biochemical fields of study. This contribution focuses on the electrochemical and photochemical properties of $[Ru(bpy)_2dcb]Cl_2$ monolayers and their subsequent use for the detection of amino acids, e.g. proline. The ability of such a complex to form stable monolayers enables its utilization for the detection of oxalate and several amino acids, producing ECL emissions following similar reaction schemes. The stability and reproducibility of these layers shows great potential for its incorporation into ECL sensor design for the detection of amino acids and possibly some peptide compounds. Thus these $[Ru(bpy)_2dcb]Cl_2$ monolayers could substantially improve limits of detection while reducing the amount of complex needed for the analysis leading to greener chemistry. Under optimised conditions, the response linearly increased with the concentration over the concentration range $0.2 \leq [\text{Proline}] \leq 1$ nM while for hydroxy-proline the dynamic range is from 1 to 10 nM with a correlation coefficient of 0.9998 and 0.9968 respectively. The ECL signal was monitored at ~ 644 nm, representing the $\lambda_{max}$ for the $[Ru(bpy)_2dcb]Cl_2$ monolayers. This wavelength is shifted by approximately 28 nm compared to the photoexcited $\lambda_{max}$ for the same system. The monolayers showed excellent stability with the response decreasing by less than 8% after continuous scanning over 4 hours.

The monolayers were formed by direct interaction with the electrode surface without the need for surface modification or chain linkers. This is a major advantage for the fabrication of any sensor as it reduces the synthesis times resulting in more economically and cheaper production costs. This technique is simple, rapid, selective and sensitive, and shows potential for the high-throughput quantitation of amino acids if adapted with other techniques such as FIA or LC systems.

# Manufacturing of Semiconductor – Oxide Nanocomposites Based on Indium Phosphide

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Problems, associated with electrochemical dimensional treatment and electroless deposition as method of manufacturing nanocomposites based on the $A^{III}B^{IV}$ semiconductors, are considered by studying indium phosphide (n-InP).

Nanoporous n-InP manufactures by electrochemical etching in an aqueous solution of HCl. Pores 80 – 100 nm in diameter are well orientated normally to the surface. The basic quantitative characteristic of the obtained structure is the aspect ratio A.=h/d, where h and d are pore's depth and diameter. It is shown possibility of manufacturing nanoporous layers of n-InP with A ~ 500. These layers ware subjected to electroless deposition oxides (Cu and Ag) into pores. Prior to plating we activated the surface by means of successive processes of sensitization and treatment in a solution of palladium chloride (for oxide Cu) and tin dichloride ( for oxide Ag).The interplay between the electroless deposition kinetics and uniformness of manufactured layers, as well as the degree of nanopores` filling was analysed. Chemical composition and morphology of the samples' surfaces, as well as concentration distribution of elements inside pores (on freshly cleaved cross sections) are determined by SEM (TESCAN) and EDX.

It is shown that uniformity deposition is defined by the electroless deposition rate. A relatively high oxide copper deposition rate (glycerate solution of the electroless deposition Cu) pertaining to the manufacturing of oxide Cu – InP leads to a low uniformity deposition, as a consequence to a low level of the pores` filling. The raising of uniformity is provided by decreasing of temperature. Conversely, the substantially lower rate of the silver chemical deposition from a triethanolamine – containing solution leads to a better uniformity of deposition and to a higher degree of the pores` filling.

Model for qualitative description of metal distribution inside pores are presented.

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# A cholesterol biosensor based on magnetic nanoparticles

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Recently there has been an increased interest in nanosize magnetic materials due to their possible applications in sensing. Magnetite ($Fe_3O_4$) is a well-studied super-paramagnetic material and magnetite nanoparticles may be synthesied using various techniques. The method employed in this study involved chemical co-precipitation of iron(II) and iron(III) chloride (1:2), allowing separation of the nanoparticles in solution due to their magnetic character. Properties depend on particle size, particle-matrix interactions and dispersion within the matrix. Their biocompatibility, low toxicity and ease of preparation allows such nanoparticles to be applied to the immobilisation of biological entities. In this study such nanoparticles were applied to the development of a novel cholesterol biosensor based on immobilised cholesterol oxidase and esterase using covalent attachment via 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide (EDC). The analytical performance parameters of the nanoparticle modified electrode bound to cholesterol oxidase was evaluated using amperometry and resulted in linearity up to 1.4 mM, sensitivity of 1.5 μA/mM and LOD of 23 μM. Lineweaver-Burk plots ($r^2$ = 0.9996) resulted in a $K_m$' of 24.9mM. Total cholesterol sensors were prepared with the inclusion of cholesterol esterase and using cholesteryl palmitate as substrate for the two enzyme system and resulted in linearity up to 1 mM, sensitivity of 1.15 μA/mM and LOD of 1 μM. The complex $[Os(bpy)_2(pic)]Cl$ (where pic is picolinic acid, byp is 2,2 bipyridyl) which acts as a mediator for glucose oxidase, was synthesised and characterised and incorporated into the nanoparticle/enzyme layer. Cyclic voltammetry showed the redox couple $Os^{2+}/Os^{3+}$ with surface coverage 2.5 $\times 10^{-9}$ mol/cm$^2$ with average percentage loss in electroactivity of 10%. Upon addition of substrate there was an increase in the oxidation current as a result of the interaction of the oxidised $Os^{3+}$ with the reduced cholesterol oxidase enzyme. Amperometry was carried out at $E_{app}$ = 0.3 V (vs. Ag/AgCl) with linearity up to 0.3mM, sensitivity 20.6 nA/mM and LOD 2 μM.

# Improved safety behavior of $Li_xCoO_2$ encapsulated by cobalt phosphate nanoparticle for lithium ion battery

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In pace with the capacity and cycle life improvement of lithium ion battery it requires serious look into the safety aspect of the battery as millions of laptop batteries were recalled during 2006 by computer manufactures due to sporadic incidence of cell rupture and sudden explosion. We present here how the nano particle coating over LiCoO2 has improved the stability of the pouch cell and explain the cause for its stability during abuse condition. We have chosen a commercial pouch cell (1Ah) of dimension 60x33x4mm$^3$ and evaluated their thermal behaviour by subjecting them to over charge and also nail penetration tests. We received cells from a manufacturing concern and their data on these cells reveal that the cathode material is coated over aluminium foil current collector. Cathode material is a blend consisting of active material LiCoO2 (94%), Super pure black (SPB, 3%) a conducting material and polyvinylidene difluoride (PVDF, 3%) the binder. The anode is a carbon (Mesocarbon microbead) and PVDF coated over copper foil. Cells with and without nano-cobalt phosphate particle coating over $Li_xCoO_2$ were chosen for safety tests. Both the cells have $Li_xCoO_2$ particle size 10µm thick. The thickness of the cobalt phosphate coated over the cathode[1] is around 20 nm. The nano-particle coated and uncoated cells were first subjected to over charge test. The overcharge test was carried out by charging both type of cells separately at 1 A(1C rate) current and observed the maximum time taken to reach the maximum temperature before cell failure. After reaching a certain maximum temperature and voltage, the cell voltage drops abruptly. The cell with uncoated cathode reaches 108°C in 130 minutes at which the cell voltage is 7.5V. But the cell with coated one reaches 62°C in 150 minutes. On comparing the peak temperature 108°C of nano-particle coated cathode with the peak temperature 62°C of uncoated cathode one may understand how safe the lithium ion battery with nano-particle coated cathode material under abuse conditions. The stability of the battery with cobalt phosphate nanoparticle coated cathode is ascribed as due to the low solubility of $Li_xCoO_2$ and reduced concentration of cobalt in the electrolyte. It is also presumed that the nano-coating, in addition to shielding the cathode it also provides ionic pathway for lithium ion conduction through the high Brunauer-Emmett-Teller(BET) surface area of the coating material[2]. Cho et al have carried out extensive work on nanoparticle coating on $Li_xCoO_2$ and reported[3] that optimum coating thickness is 10-15nm.

1) Hyunjung Lee, Min Gyu Kim, Jaephil Cho, Electrochem. Commun.9 (2007) 149.
2)Y. J. Kim, H. Kim, B. Kim, D. Ahn, J.G. Lee, T. J. Kim, D. Son, J. Cho, Y.-W. Kim,and P. Park, Chem. Mater., 15, 1505 (2003).
3) J. Cho, Y.W. Kim, B. Kim, and B. Park, Angew. Chem., Int. Ed., 42, 6181 (2003).

# Nano layer $Co_3(PO_4)_2$ coated $Li_xCoO_2$ for High performance lithium-ion battery

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The expanding electronics miniature application requires compact high performance lithium-ion batteries which resulted in most probable areas of development such as improvement of energy density of the active material through identification of proper dopant, development of nanoparticle electrode active material, encapsulation of the electrode by polymer coating, and nanoparticle coating over electrode active materials. We have considered investigation on nanoparticle coating over electrode active materials, especially 20nm thick coating of $Co_3(PO_4)_2$ on 10μm $LiCoO_2$ cathode particle through mixing of the respective salts in distilled water followed by heat treatment[1]. Cycle life and capacity behaviour of nanoparticle coated cathode was compared with uncoated cathode containing cell. 1Ah capacity commercial cells manufactured in a company were considered for this study. Its dimension is $60x33x4mm^3$. The data provided by the Company illustrates that the cathode material is a blend of active material $LiCoO_2$ (94%), Super pure black (SPB, 3%), and polyvinylidene difluoride (PVDF, 3%) coated over aluminium foil. The anode is a mix consisting of carbon (Mesocarbon microbead) and PVDF coated over copper foil. Both types of cells were subjected to charge and discharge cycling with cut off voltages 4.35 and 3V respectively. The 1st and 300th discharge capacities of cell with nanoparticle coated cathode are 1.30 and 0.79Ah and cell with uncoated cathode are 1.20 and 0.68Ah respectively. These results show that nano coated cathodes show better performance compared to uncoated $Li_xCoO_2$ cathode. Application of metal phosphates in the area of batteries is of recent origin compared to the fields such as molecular sieves, size-selective, optical materials etc[2]. Nanoparticle metal phosphates such as $AlPO_4$ and $Co_3(PO_4)_2$ coated over $LiCoO_2$ has been extensively investigated[3-5]. Cho et al explains that $AlPO_4$ coating exists over $LiCoO_2$ particle as an intact cover whereas $Co_3(Po4)_2$ coated over $Li_xCoO_2$ undergoes a chemical reaction resulting in the formation of ~7nm thick $LiCoPO_4$ coat over $LiCoO_2$. This $LiCoPO_4$ olivine phase is responsible for providing excellent cycle life, high capacity and high operating voltage compared to the cells consisting of uncoated cathode. Further investigations on nanoparticle coated $LiCoO_2$, especially on its stability, thermal and structural aspects are under way so as to further improve the capacity and safety aspect of the lithium ion battery

1)H.J. Lee, M.G. Kim, J.P. Cho, Electrochem. Commun., 9 (2007) 149.
2)C.N.R.Rao et al., Acc. Chem. Res., 34 (2001) 80.
3)A.Dong et al., J. Am. Chem. Soc., 125 (2003) 4976.
4)Y. J. Kim et al., Chem. Mater., 15, 1505 (2003).
5) J.P. Cho et al., Angew. Chem., Int. Ed., 42, 6181 (2003).

# Synthesis and Electrochemical Evaluation of $La_{1-x}Sr_xCoO_3$ Cathode Material for Zinc Air Batteries Application

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We synthesized nano-sized $La_{1-x}Sr_xCoO_3$ (x=0.1~0.4) cathode catalyst for the zinc air secondary batteries by citrate method and measured cathode's electrochemical characteristics according to content of strontium compose the cathode catalyst. We controlled the pH of precursor solution by 2 and 10 respectively in the process of manufacturing the precursor. We heat treated the prepared precursor at various calcination temperature (500~900 ), and examined the optimum calcinations temperature by XRD analysis and electrochemical evaluation.

We examined the ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) performance of the prepared $La_{1-x}Sr_xCoO_3$ catalyst powder. When we consider ORR and OER performance simultaneously, $La_{0.7}Sr_{0.3}MnO_3$ catalyst has shown the best performance because of its lowest voltage deference between charge and discharge

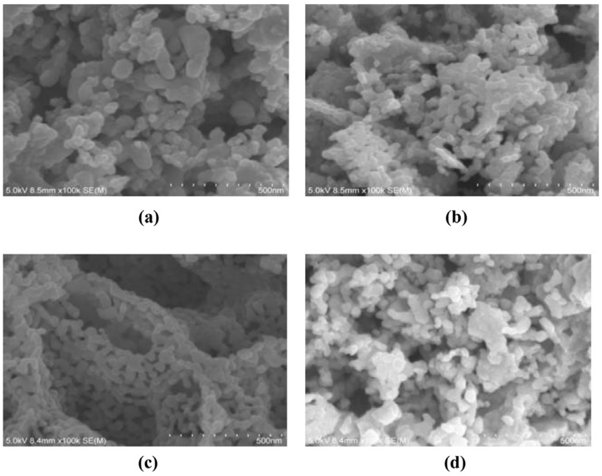

Fig. 1 SEM images of the $La_{1-x}Sr_xCoO_3$ catalyst.
(a) x = 0.4 (b) x = 0.3 (c) x= 0.2 (d) x=0.1

# Electron Transfer in Substituted Polynuclear Platinum Derivatives. Spectroelectrochemical and Theoretical Studies

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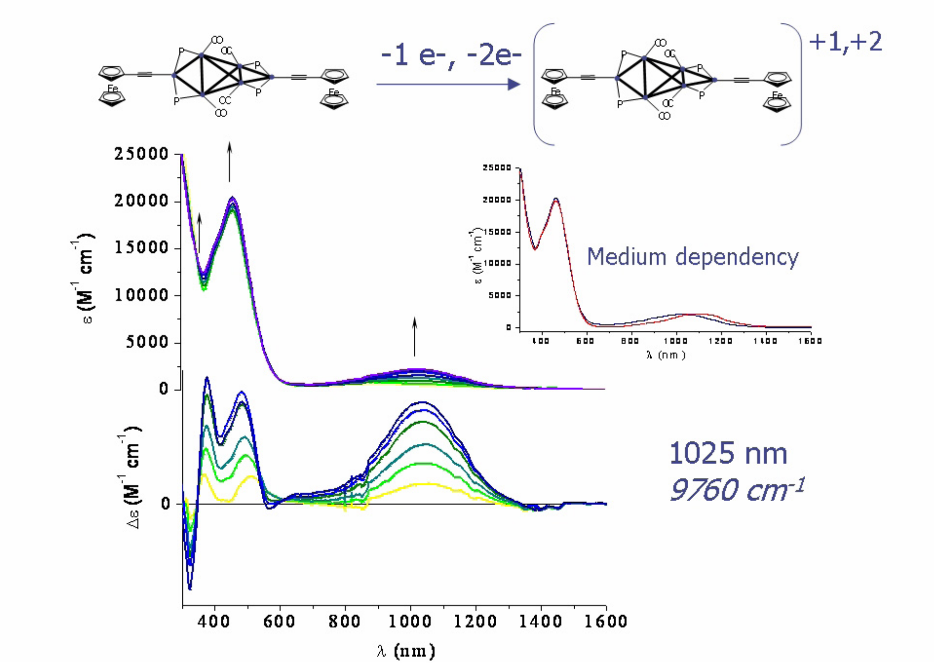
Ferrocenyl groups are frequently attached to organometallic or coordination compounds, however examples of metal clusters capped by equivalent ferrocenyl groups are rare. We will discuss here on electronic properties of a series of complexes, in which a tri- or hexa-platinum core ($[Pt_3(\mu\text{-}PBut_2)_3(CO)_2]^+$ or $[Pt_6(\mu\text{-}PBut_2)_4(CO)_4]^{2+}$) is capped by one or two ferrocenylethynyl groups, displaying a photoelectrochemically triggered electron transfer from the $Pt_n$ core to the peripheral Fc subunit(s). TDDFT calculations and the effect of solvent on the calculated spectra will be presented.



To the best of our knowledge this is the first example in which a metallic cluster behaves as electron donor versus a ferrocenium acceptor.

# Towards label free DNA sensing through semiconducting nanowires

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We report the results of an innovative electrical detection of biological binding, which is based on a thin SnO2 film, acting as the channel of a field effect transistor. The working principle does not rely on modulation of an enriched/depleted Si channel like in chem-FETs, but of a Metal Oxide (MOX) space charge region (SCR) size like in a JFET. The feasibility of the working principle was at first demonstrated by pH measurement in liquid. Afterwards we implemented a protocol for nucleic acid derivatization of SnO2, which proved reliable for the immobilization of ODNs and electrical sensing of hybridization.

The results obtained on macroscopic structures prompted the development of nano biotransistors based on single nanowires of metal oxides. Quasi one-dimensional nanostructures offer the greatest chance yet for creating robust, sensitive and selective electrical detectors of biological binding events. Biological macromolecules bound to the surface of a nanowires and undergoing a binding event with conformational change or change of a charge state, may thus perturb the current flow in the nanowires as already shown on Si nanowires . The well known high reactivity of metal oxides surfaces make them candidates to develop much more sensitive DNA and protein sensors than Si nanowires. A simple process to realize a device based on a single $SnO_2$ nanowire has been designed and derivatization by Dip Pen Nanolitography explored. On single crystal MOX nanowire transistors, drift due to surface hydration and ions diffusion is expected to be negligible.

Keywords Nanobiotechnology, Semiconductor Oxide Nanobelts, Silicon, Carbon Nanotubes, Microelectronic Technologies, Dna Biosensor, Hybridization, Genetically Modified Organisms, Nanomanipulation

# Orientation of a Self-Assembled Monolayer of Decanethiol on Au(110) as monitored by Reflection Anisotropy Spectroscopy

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Reflection Anisotropy Spectroscopy (RAS) is an optical technique which, when used with cubic substrates, is a very powerful real-time monitor of surface structures. Being an optical technique, RAS can be used in any environment which is transparent to the wavelength range of the spectrometer, and as such it can readily be employed in many liquid environments. When a sample is rotated through θ degrees, the RAS signal from surface bonds varies as 2θ. A self assembled monolayer (SAM) of decanethiol on Au(110) was prepared by incubating a 0.1M solution of decanethiol in ethanol on Au(110) for 5 minutes then washing with phosphate buffer pH7. The sample was then rotated in the buffer. This enabled the orientation of the decanethiol with respect to the principal axes in the Au(110) surface to be estimated. By selecting the Au-S bond and comparing its rotation response with that from bonds in the Au (110) it is seen that there is a projection of the Au-S bond in the (110) plane which is oriented some 8 degrees with respect to the Au(110) principal directions. This is compared with STM results on similar systems.

# Ac-Electrogravimetry Characterization of Poly[Pd(3-Mesalen)] Electroactive Thin Films

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Metal(*salen*) based polymers (M=Ni, Cu, Pd) are novel soft materials[1,2] with potential applications as electrochromic and photochemical systems and as electrochemical sensors due to their relevant electro/photochemical and optical properties.[1,2] The understanding of the transport of charge and neutral species during their redox processes is, consequently, of crucial importance.

Ac-electrogravimetry is a technique which, combining electrochemical impedance and electrochemical quartz-crystal microbalance, has been used to study the mobile species involved in the redox switching of conducting polymers.[3,4] This technique allows the separation of solvent, cations and anions transfer at polymer/electrolyte interface, due to their different time constants of relaxation.

In this work ac-electrogravimetry is used to characterize the redox process of thin electrogenerated [M(*salen*)]-based films. Electrochemical impedance and ac-electrogravimetric transfer functions were carried out on poly[Pd(3-Mesalen)] films as a function of different applied potentials, anions, cations and solvent.

The poly[Pd(3-Mesalen)] films were always prepared by potential cycling, between -0.1 and 1.2 V at 0,2 V $s^{-1}$, in acetonitrile solutions containing the monomer ≈ 1 mmol.$dm^{-3}$ and 0.1 mmol.$dm^{-3}$ TBAP, using a three electrode cell with 10 MHz AT-cut quartz crystal plated with a platinum film as working electrode, Pt counter electrode and an Ag/AgCl (1 mol $dm^{-3}$ NaCl) reference electrode. Electrochemical impedance and ac-electrogravimetric studies were then performed using the same solvent/supporting electrolyte as in the polymerisation and using other supporting electrolytes: $TBAPF_6$, $TBABF_4$ and TEAP.

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References

1. M. Vilas-Boas, M. J. Henderson, C. Freire, A. R. Hillman, E. Vieil. *Chem. Eur. J.* **2000**, 6, 1160-1167.
2. M.Vilas-Boas, I. Santos, M. J. Henderson, C. Freire, A. R. Hillman, E. Vieil. *Langmuir* **2003**, 19, 7460-7468.
3. C. Gabrielli, J. Jareno, M. Keddam, H. Perrot, F. Vicent. *J. Phys. Chem. B* 2002, 106, 3182-3191.
4. C. Gabrielli, J. Jareno, M. Keddam, H. Perrot. J. Electroanal. Chem. 2000, 485, 101-113.

# Development of a biocatalytic fuel cell working in physiological conditions.

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A biofuel cell[1] consisting of a glucose oxidase-based anode and a laccase-based cathode using osmium-based redox polymers as electron transfer mediators between enzymes and electrode surfaces has been studied.[2] The electrodes are modified by deposition of appropriate enzyme and redox polymer mediator. An osmium redox polymer of moderately low redox potential is used for the glucose oxidizing anode and an osmium redox polymer of moderately high redox potential is used for the dioxygen reducing cathode. The working biofuel cell is been studied under air at 37°C in a 0.1 M phosphate buffer solution of pH range 4.4 to 7.4, containing 0.1 M sodium chloride and 10 mM glucose. Under physiological conditions (pH 7.4) maximum power density, evaluated from the geometric area of the electrode, reached 16 $\mu W/cm^2$ at a cell voltage of 0.25 V. At lower pH values maximum power density was 40 $\mu W/cm^2$ at 0.4 V (pH 5.5) and 10 $\mu W/cm^2$ at 0.3 V (pH 4.4).

In order to operate in a physiological buffer, the immobilized enzyme activity and stability need to be improved (our laccase has a low activity at pH 7.4 and the cell was not stable in time). Covalent coupling of enzymes and mediators on the electrode surface can appreciably improve the fuel cell stability. Also, improvements in the design of the redox polymers (in terms of structure and redox potential) help to increase the biofuel cell power output.

We present different approaches aimed at improving the stability and the power output of the biofuel cell working in pseudo-physiological conditions, including redox polymer design and synthesis, surface modification, enzyme selection, electrode structure and refinement of the immobilisation procedure.

1. A. Heller, *Phys. Chem. Chem. Phys*., 2004, 6(2), 209
2. (a) F. Barrière, Y. Ferry, D. Rochefort, D. Leech, *Electrochem. Com*., 2004, 6(3), 237. (b) F. Barrière, P. Kavanagh, D. Leech, *Electrochim. Acta* 2006 (51) 5187

# In-situ probing of dynamic nano-structural change of electrodeposits in course of oscillatory growth using SERS

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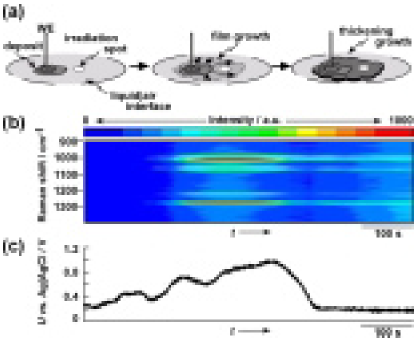
Electrochemical reactions in oscillating system proceed spatial-synchronically under non-equilibrium conditions, showing various beautiful spatiotemporal patterns at electrode surfaces. Of various oscillations, oscillatory electrodeposition is especially interesting from the point of view of production of micro- and nano-structured materials because it has a possibility to produce ordered electrodeposits by recording ever-changing self-organized spatiotemporal patterns during the oscillation.

Here we report that dynamic nano-structural change of a gold (Au) film formed at a liquid/air interface by oscillatory electrodeposition was probed by surface-enhanced Raman scattering (SERS) under in-situ condition. The oscillatory formation of the Au film was explained by taking into account that the electrodeposition proceeded under diffusion-limited conditions when the potential shifts to the positive during the potential oscillation, whereas it proceeded under reaction-limited conditions during the negative potential shift. Ex-situ SEM inspections of the deposits formed under oscillatory conditions revealed that each potential shift is accompanied by growth of needle-like nano-crystals and formation of a continuous film via the thickening and coalescing of the nano-needles, respectively. The SERS intensity was high when the potential moves from the negative end to the positive end of the oscillation, whereas it became lower when the potential moves from the positive to the negative end, clearly indicating that the SERS probes the dynamic nano-structural change from the nano-needles into a continuous film of the deposits in the course of the oscillatory electrodeposition.



(a) Schematic illustrations to explain how the SERS signal was measured in-situ. (b) Raman spectrum as a function of time. (c) One cycle of the potential oscillation measured concurrently with the measurement of spectrum (b).

**Reference**
Saliba, R.; Mingoutaud, C.; Argoul, F.; Ravaine, S.; *J. Electrochem. Soc.,* **2003**, *150(3),* C175-C183.

# Electrochemical detection of DNA hybridization using antinomycin D and redox mediators

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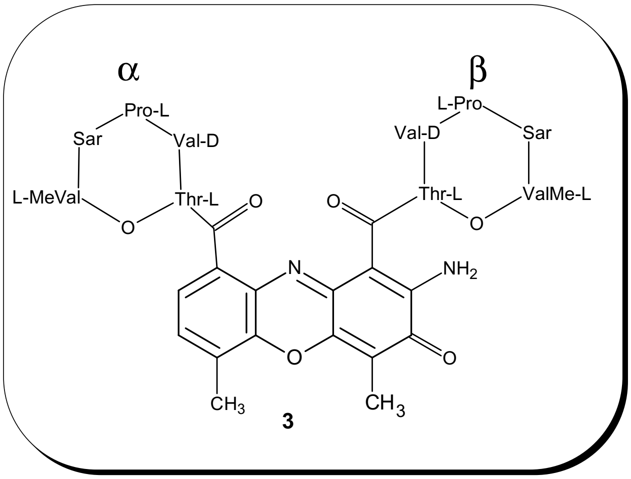
Electrochemical detection of DNA hybridization is either based on monitoring the redox response of a DNA-attached redox mediator or on oxidation of guanine residues which is hindered after hybridization. In addition, recently a number of electrochemical strategies for detection of DNA hybridization were proposed [1]. Besides the evaluation of the guanine oxidation current, which is decreasing upon hybridization, an additional decrease of the current can be observed after intercalation of suitable compounds within the double-stranded DNA.

Actinomycin D (ACTD; see scheme 1) is an antitumor antibiotic that contains a 2-aminophenoxazin-3-one chromophore and two cyclic pentapeptide lactones. The chromophore is intercalating with high binding constant into double-stranded DNA preferentially at GC-Watson-Crick base pairs.

In this work, the interaction between ACTD and single as well as double stranded DNA is studied in the presence of different types of redox mediators. For this purpose, thiol-modified ss-DNA is immobilised on a Au ultramicroelectrode, and the electrochemistry of the redox mediators in the presence and in the absence of ACTD is investigated using cyclic voltammetry.

The entire procedure is repeated after hybridization of the surface bound DNA sequence with its complementary strand.

The modulation of the electrochemistry of different redox mediators is used as a positive response to identify productive hybridization.



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Scheme 1: Structure of ACTD

Moreover, the electrochemical properties of ACTD either as free-diffusing or intercalated compound are investigated. Based on these results, new strategies for the detection of DNA hybridization will be discussed.

[1] Palecek, E., Scheller F., Wang, J., eds. Electrochemistry of nucleic acids and proteins – Towards electrochemical sensors for genomics and proteomics

# Blood Lead Analysis Using Nanostructured Screen-Printed Carbon Electrodes

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In this work, the surface of screen-printed carbon electrodes is modified with gold to get a nanostructured surface. The voltammetric behaviour of these nanostructured screen-printed carbon electrodes is studied.

The surface of the electrodes is modified in two different ways; by evaporation of a colloidal gold suspension on the electrode previously activated in basic media, or by gold electroplating applying a constant current.

The nanostructured screen-printed carbon electrodes constructed with the optimised experimental conditions are used for the electrochemical determination of lead in aqueous medium using anodic stripping square wave voltammetry. A shift of the potential of the anodic peak of lead towards more positive potentials is observed when screen-printed carbon electrodes are modified with gold. The analytical characteristics as limits of detection, linear ranges, reproducibility and the selectivity of the determination of lead in aqueous medium using these nanostructured screen-printed carbon electrodes are evaluated.

Finally, these nanostructured screen-printed carbon electrodes will be used for blood lead analysis using an internal standard.

This work has been supported by the Project BIO2006-15336-C04-01

# Carbon Paste Electrodes Modified with a new Phenothiazine Derivative Adsorbed on Zeolite and on Mineral Clay for Nadh Oxidation

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Zeolite and clay modified electrodes have been widely investigated during the last two decades. The zeolites have very attractive characteristics for immobilization of electroactive species used as mediators for electron transfer processes [1], and, at the same time, they have chemical, physical and structural characteristics (shape and size selectivity, physical and chemical stability, high ionic exchange capacity and hydrophilic character) of high interest in electroanalytical chemistry [2]. On the other side, clays are often used as efficient matrices for biomolecules and/or electrocatalysts immobilization [3]. That is way the use of zeolites and mineral clays is of interest for obtaining modified electrodes with electrocatalytic activity for NADH oxidation [4].

Continuing our preoccupation in this domain [5], the physical-chemical, electrochemical and electrocatalytic behaviour towards NADH oxidation of two new modified electrodes have been investigated. These electrodes are based on carbon paste, which incorporates two different materials for mediator (a new phenothiazine derivative, 3,7-di(m-aminophenyl)-10-ethyl phenothiazine, **EPh**) immobilization: a synthetic zeolite (**Z**) (13X type, from Aldrich) and a mineral clay (**B**) (bentonite, from Chioarului Valley, Maramures county, Romania). Both electrodes were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X Ray Spectroscopy (EDS), Fourier Transform Infrared (FTIR) Spectroscopy, cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements.

CV investigations, performed at different scan rates in aqueous phosphate buffer solutions, allowed estimation of the heterogeneous electron transfer rate constant ($k_s$) by using Laviron method. Using Koutechy-Levich approach, the second-order rate constant for electrocatalytic oxidation of NADH ($k_{obs}$) was also evaluated. The $E^{0'}$ of **EPh** adsorbed on zeolite (**EPh-Z-CPEs**) and bentonite (**EPh-B-CPEs**) incorporated in carbon paste was found pH independent.

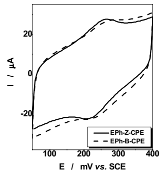

**Figure 1.** Cyclic voltammograms corresponding to EPh-Z-CPEs and EPh-B-CPEs. Experimental conditions: starting potential, 50 mV *vs.* SCE; scan rate, 50 mV $s^{-1}$; supporting electrolyte, 0.1 M phosphate buffer, pH 7.

**References**

[1] A. Walcarius, C. R. Chimie, 8 (2005) 693.
[2] A. Walcarius, Anal. Chim. Acta, 384 (1999) 1.
[3] I. K. Tonle, E. Ngamenib, A. Walcarius, Electrochim. Acta, 49 (2004) 3435.
[4] L. Gorton, E. Domímguez, Rev. Molec. Biotechnol., 82 (2002) 371.
[5] D. Gligor. L. Muresan, A. Dumitru, I. C. Popescu, J. Appl. Electrochem., in press.

# Development of a CNT paste electrode $Os^{2+/3+}$ polymer-mediated biosensor for determination of glucose in alcoholic beverages

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A new mediated carbon nanotube paste (CNTP) amperometric biosensor for glucose is described. The biosensor is based on the activity of two commercially available enzymes, NAD-dependent glucose dehydrogenase (GDH) and diaphorase (DI) and is realized through co-immobilising both enzymes, a mediator (two different osmium functionalised polymers were investigated, one with an E°' of +140 and another with –195 mV vs. Ag|AgCl) and $NAD^+$ on the electrode surface. The mediator was demonstrated to shuttle the electron transfer between the immobilised diaphorase and the CNTP electrode, thus showing a good electrocatalytic activity towards NADH oxidation at potentials around either +200 or at around –150 mV vs. Ag|AgCl, where interfering reactions are less prone to occur.

In a preliminary phase, all important analytical parameters such as enzymes, co-enzyme and mediator immobilization concentration, pH, temperature and probe lifetime are studied and optimized.

Using the high potential Os-polymer, the biosensor exhibits a detection limit of 10 µmol $L^{-1}$, linearity up to $8x10^{-4}$ mol/L, a sensitivity of 13.4 µA $cm^{-2}$/mmol $L^{-1}$, and using the low potential Os-polymer the biosensor exhibits a detection limit of 3 µmol $L^{-1}$, linearity up to $10x10^{-3}$ mol/L, a sensitivity of 21 µA $cm^{-2}$/mmol $L^{-1}$. Both systems showed a good reproducibility (RSD 2.1-3 %, n=6) and a stability of about 1 week when stored dry at 4°C.

Finally, the proposed biosensor was applied for the determination of glucose in different samples of sweet wine and validated with a commercial spectrophotometric enzymatic kit.

# Development of an electrochemical alcohol oxidase biosensor based on carbon nanotube modified carbon film electrodes

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During the last 15 years carbon nanotubes (CNT) have attracted enormous interest due to their unique structural, mechanical and electronic properties. Preparation, purification, solubilisation and possible application of CNT have been extensively investigated [1]. The major problem to develop the electrochemical CNT based sensors and biosensors is the insolubility of CNT in all solvents. Various strategies have been used to minimize this problem either through covalent modification or noncovalent funcionalisation [2].

Carbon film electrodes made from carbon film electrical resistors [3] exhibit better electrochemical properties and a wider potential window than many other carbon electrodes, after surface pretreatment. They have been used for electrochemical sensors, e.g. [3,4] and redox-mediated biosensors, e.g. with poly neutral red [5].

A casting method for multi-walled CNT (MWCNT) was first investigated, based on methods developed on glassy carbon electrodes. The MWCNT were functionalised in $HNO_3$, then dissolved in Nafion, dimethylformamide or cellulose acetate. The same casting methods were tested with carbon film electrodes with good results, but due to the low volume required for electrode modification the reproducibility was not sufficiently good for comparative studies. For this reason, functionalised MWCNT were directly attached to the carbon film electrodes without solvent.

The MWCNT/carbon film electrode was successfully tested as a glucose biosensor based on glucose oxidase (GOx) using immobilisation of a GOx-BSA (bovine serum albumin) mixture on top of the MWCNT. It was then applied to the development of an alcohol biosensor based on alcohol oxidase (AlcOx), using drop-coating on the MWCNT/carbon film of an enzyme layer with AlcOx-BSA and glutaraldehyde cross-linking. The properties of this biosensor were evaluated and interferences studied. Electrocatalytic effects and the increase in sensitivity compared with biosensors based on unmodified carbon film electrodes will be discussed.

[1] J.J. Gooding, *Electrochim. Acta* **2005**, *50*, 3049.
[2] J. Wang, M. Musameh, Y. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 2408.
[3] C.M.A. Brett, L. Agnes, H.D. Liess, *Electroanalysis* **2001**, *13*, 765.
[4] C. Gouveia-Caridade, C.M.A. Brett, *Electroanalysis* **2005**, *17*, 549.
[5] M.E. Ghica, C.M.A. Brett, *Electroanalysis* **2006**, *18*, 748.

# Role of Rigidness of the Matrix in Electrochemical Matrix Synthesis of Interpolymer Complexes of Polyaniline with Polysulfonic Acids of Various Nature

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Polyaniline films were prepared by the electrochemical matrix polymerization of aniline in the presence of the following polyamidosulfonic acids: poly(2-acrylamido-2-methyl-1-propanosulfonic acid) (PAMPSA); poly-p,p'-(2,2'-disulfoacid)-diphenylen-iso-phthalamid (i-PASA); poly-p,p'-(2,2'-disulfoacid)-diphenylen-tere-phthalamid (t-PASA) and a copolymer of the latter two, poly-p,p'-(2,2'-disulfoacid)-diphenylen-iso-phthalamid-co-p,p'-(2,2'-disulfoacid)-diphenylen-tere-phthalamid (co-PASA). The matrix polymerization results in formation of the interpolymer complexes of polyaniline (PAn) and the above cited polyacids. The course of polymerization was studied by UV-Visible spectroscopy, chronoamperometry and the results were compared with common synthesis in inorganic acid (HCl).

We observe the acceleration of aniline polymerization in the presence of polyamidosulfonic acids. The polyaniline synthesis on the polyacids proceeds at higher rate (as compared HCl) owing to a high degree of association of aniline on the polyacids, which ensures high local concentration of aniline and hydrogen ions in the vicinity of a polyacid molecule. Along with this, the characteristic features of spectral changes and the polymerization rates depend strictly on the structure of polyacid matrix, and, in the case of PAMPSA (and HCl), on the concentration..

The acceleration of the polymerization in the presence of polyamidosulfonic acids results in the improvement of the morphology and uniformity of the electropolymerized film.

Polyaniline films exhibited good electrochemical stability and high adherence to $SnO_2$-glass substrates. According to CVA and spectroelectrochemical data the formation of the quinoid units in the interpolymer complexes PAn with rigid polyacids is retarded, while flexible polymer matrixes possess spectroelectrochemical properties very similar to those of conventional PAn. So, the structure of rigid polymer matrix determines the structure of the interpolymer complex with PAn and thus disturbs its characteristics, while flexible polymer matrix can adopt its structure to the structure of polyaniline.

The difficulties in the formation of quinoid structures in PAn-PASA films also results in more intensive absorption of the electrochemically synthesized PAn-polyamidosulfonic acids films in the near-IR spectral range (absorbance of the charge carriers) in comparison to the absorption of common PAn films.

# The Role of Pt-Ru-Pd Nanoparticles Dispersed on Poly(3-Methyl) Thiophene Conducting Polymer on the Electrooxidation of Methanol

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Direct Methanol Fuel Cell (DMFC) is an ideal power source for electric vehicles because of favourable properties of methanol as a fuel. Methanol is a liquid which can be easily stored, handled and produced from oil,natural gas,coal or biomass. Thus,it should be widely available and cheap. Morever,the DMFC can run at low temperatures (around $100^0$C) and does not require fuell processing.

For a long time, platinum was considered as the best electrocatalyst in acidic medium for methanol oxidation in terms of fuel cell application. However, the methanol oxidation at a platinum electrode is a self-poisoning reaction, owing to strongly adsorbed $CO_{ads}$ or $COH_{ads}$ by chemisorption of methanol. In order to enhance the performance of the platinum electrode, one way is to increase the active surface area by dispersion of the catalyst as small particles on a convenient conducting support. This can be achieved by the use of a conducting polymer such as polythiophene, polypyrrole or poly aniline.

The use of bimetallic catalysts such as Pt-Ru improves the performance of practical electrodes and decrease poisoning. Moreover, the preliminary experiments have shown that the incorporation of a third metal to the binary catalyst enhanced the performance of methanol oxidation compared to Pt-Ru, at low potentials.

In this study, the electrochemical oxidation of methanol was investigated on Pt-Ru-Pd nanoparticles dispersed on poly-3-methyl thiophene (P-3MeT) polymer matrix. The catalysts were prepared by electrochemical deposition and dispersed in a conductive three-dimensional matrix, an electronic conducting polymer (P-3MeT). The performance of ternary catalyst on methanol oxidation was compared to that of binary catalyst under the same experimental conditions. The anode compositions and morphologies were verified using SEM, TEM and XPS technique.

References

[1] Gotz, M. And Wendt, H**.,** *Electrochim.Acta.*,43,3637, 1998.
[2] Swathirajan, S. And Mikhail, YM**.,** *J. Electrochem.Soc.*,139, 2105-2110, 1992.
[3] Lima A.,Coutanceau C., Leger J.M. and Lamy C., *J. Appl. Electrochem.* 31, 379, 2001.
[4] Guney S., Becerik I. and Kadirgan F., *Bull.of Electrochem.* 20,157, 2004.

# The Electrocatalytic Behaviour of Oxygen Reduction Reaction at Nano Size Conducting Polymer Electrodes Modified by New Water-Soluble Cobalt Phthalocyanine Derivatives

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Oxygen reduction is a cathode reaction in fuel cells, potentially efficient, emission free energy source. The reaction should occur at a low potential for efficient energy production. It is desirable that the reaction goes to completion and forms water via a four electron transfer mechanism. However, oxygen gets reduced to hydrogen peroxide via a two electron process but the peroxide can still get reduced further via another two electron process to form water. Platinum electrocatalyses the reduction of oxygen to water in fuel cells [1, 2]. Because Pt is an expensive metal, an alternative electrocatalysts have been examined. Metallophthalocyanines (MPcs) have received great attention for the oxygen reduction reaction hence their conductivity and their abilities to reduce dioxygen. The catalytic performance of MPc complexes depends on the central metal, ligands and support [3-6] The setbacks of MPc complexes as electrocatalysts for reduction of oxygen include promotion of two electron (instead of four) transfer process yielding hydrogen peroxide . However, thicker films obtained by polymerization were reported to promote four electron transfer process and are also stable[5]. In this study, a water-soluble cobalt phthalocyanine complex was newly synthesized and used as electrocatalysts for oxygen reduction. The electrode was prepared by the insertion of the water-soluble cobalt phthalocyanine into polyaniline conducting matrix during the electropolymerization of aniline. This technique of electrode preparation allowed us to obtain active and stable electrodes. The surface morphology of the catalysts was determined using SEM and the verification of the structure of modified polymer film was done by UV-vis Differential Reflectance Spectroscopy. The electrocatalytic behaviour of oxygen reduction reaction at conducting polymer film electrodes modified by new water-soluble cobalt phthalocyanine derivatives was investigated in acidic media

## .References

[1] N. Phougat and P. Vasudevan, *J. Power Sources* **69** (1997), p. 161
[2] G. Lalande, G. Faubert, R. Cote, D. Guay, J.P. Dodelet, L.T. Weng and P. Bertrand, *J. Power Sources* **61** (1996), p. 227
[3] J.A.R. van Veen and C. Visser, *Electrochim. Acta* **24** (1979), p. 921.
[4] N.P. Rodrigues, J. Obirai, T. Nyokong and F. Bedioui, *Electroanalysis* **17** (2004), p. 186. [5] Y. Tse, P. Janda, H. Lam, J. Zhang, W.J. Pietro and A.B.P. Lever, *J. Porphyrins Phthalocyanines* **1** (1997), p. 3.
[6] J. Zagal, R.K. Sen and E. Yeager, *J. Electroanal. Chem.* **83** (1977), p. 207.

# Conductive Cantilevers and Supports for Combined Atomic Force and Scanning Electrochemical Microscopy

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Insulated, conductive cantilevers are presented to study the structure-function relationship of membrane proteins in the atomic force microscope (AFM). The cantilevers exhibit electrodes with linear dimensions around 100 nm, compared with 1-10 microns for electrodes that are commonly used for scanning electrochemical microscopy (SECM). The combined AFM-SECM probes enable simultaneous access to topography and (Faraday) currents. Topographical resolution better than 1 nm has been achieved (Frederix et al. 2003, Curr. Opin. Chem. Biol. 7,641) and changes in Faraday currents have been observed with a lateral resolution of approx. 8nm.

To apply the cantilevers successfully in structural biology, the support is of importance as well. The electrochemical properties of flat, conductive supports are currently being characterized using different electrochemical methods.

# Theory vs Experiment: Electrochemical and DFT-Studies of Substituted Thiophenes

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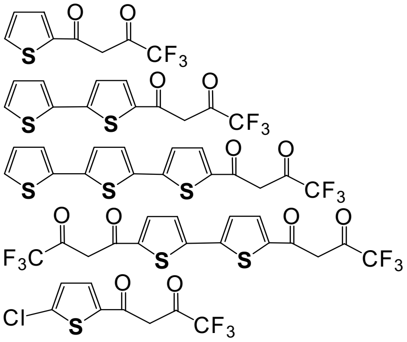
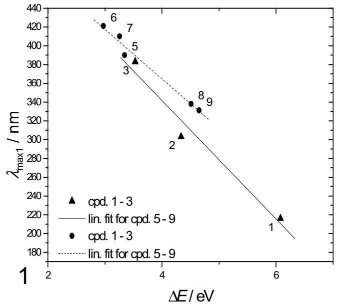
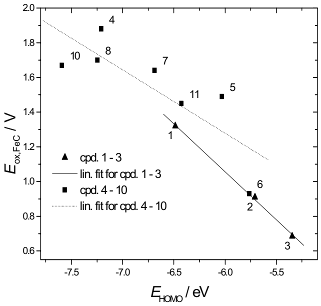
Thiophenes and their substituted relatives are well studied building blocks of intriniscally conducting polymers in electrochemistry and materials science. In inorganic chemistry, in particular in coordination chemistry, they are considered as connecting units bridging e.g. metal centers in organometallic compounds. In conceivable applications both their electrochemical response and their electrooptical properties are of interest. We have synthesized a family of substituted thiophenes (for a representative selection (cpds. **4** – **8**) see right) and studied their redox electrochemistry and UV-Vis spectroscopy. Optimization of molecular properties including tailoring for particular applications can be simplified substantially when predictive tools from theoretical chemistry are employed. We have used density functional theory DFT to calculate electron affinities and ionization potentials of the selected molecules. Comparison of obtained oxidation and reduction potentials as well as UV-Vis absorption band positions with calculated values taking into account also trends expected from known properties and influences of the employed substituents showed good agreement in most cases, in some instances limitations presumably caused by the simplifications needed to start DFT calculations (e.g. assuming the molecule in the gas phase without intermolecular and surface specific interactions) showed up suggesting the need for further research. The agreement between UV-Vis absorption maxima and calculated HOMO-LUMO energy differences is very good (below left), the same applies to the correlation between oxidation potentials and HOMO energies (below right).







# Nafion-methylene blue functional membrane and its application in biochemical sensing

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A functional membrane composed of nano particles of Methylene Blue and Nafion was constructed. The materials were characterized by the methods of SEM, TEM, UV-vis and FT-IR. The average diameter of the nano particles was estimated to be about 60 nm. The functional membrane at GC electrode showed a quasi-reversible electrochemical behavior with a formal potential, E°', of -305 ± 5 mV (vs. Ag/AgCl). The modified GC electrode was directly applicable for determining $H_2O_2$ concentration. The linear range for $H_2O_2$ determination was from $2\times10^{-4}$ to $6\times10^{-2}$ M, with detection limit of $1.2\times10^{-4}$ M. Moreover, HRP was immobilized on the MB-Nafion functional membrane. The bio-membrane modified GC electrode showed good electrochemical behavior with formal potential of -296 ± 5 mV (vs. Ag/AgCl). The resulting biosensor exhibited good stability and higher sensitivity to $H_2O_2$ relative to the membrane without HRP. The linear range of this biosensor for $H_2O_2$ determination was from $2\times10^{-5}$ to $7\times10^{-3}$ M, with detection limit of $7\times10^{-6}$ M.

# Nanostructured Pd-AAM composite membranes

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Many processes involving hydrogenation/de-hydrogenation reactions can be favourably carried out in catalytic membrane reactors, which give higher performances compared with conventional reactors. However, the use of pure Pd membranes in these reactors should be too costly, so that composite membranes, consisting of a thin palladium film deposited onto a porous support, are preferred. Anodic alumina membranes (AAM) constitute a suitable support for the palladium film, because they are easy to prepare, thermally stable and exhibit a low resistance to mass transport owing to their ordered structure. Moreover, the electrochemical procedure allows a strict control of their nanostructured morphology.

AAM were grown by anodizing Al foils in 0.4 M $H_3PO_4$ aqueous electrolyte up to 160 V, with subsequent dissolution of residual metal and barrier oxide [1]. In this work we show how morphology can be varied by changing anodizing parameters: pore length, average diameter and population on the solution-side surface change with tensiostatic charge, bath temperature and presence of $Al^{3+}$ ions in solution [2].

Composite membranes were fabricated by electroless deposition of Pd metal onto AAM. After cleaning, the porous support surface was seeded with Pd nuclei, by means of a pre-treatment consisting in an alternate sequence of sensitizing steps, performed by immersion in a $SnCl_2$/HCl aqueous solution, followed by dipping in an activation bath containing a palladium salt [3].

The deposition procedure was optimized in order to form a dense Pd layer covering pores: to limit alumina dissolution the plating bath was buffered at pH 8.5 and multiple deposition steps, each lasting 3 minutes, were performed [4]. The composite membrane formation and the ceramic support damage were monitored after each deposition step, and the effect of plating bath composition was also studied. Using $Na_2B_4O_7 \cdot H_2O$ as buffering agent, a compact Pd layer, about 1 μm thick, was obtained after 4 deposition steps alternated with surface re-activation steps. The complete pore closure was confirmed both by SEM analysis and by gas permeability measurements.

*Acknowledgements.* This work was supported financially by APQ Ricerca della Regione Siciliana: “Laboratorio dell’innovazione nel settore dei beni culturali”.

## References

[1] P. Bocchetta, C. Sunseri, A. Bottino, G. Capannelli, G. Chiavarotti, S. Piazza, F. Di Quarto, J. Appl. Electrochemistry, 32, 977 (2002).

[2] R. Inguanta, M. Butera, C. Sunseri, S. Piazza, Appl. Surf. Sci., in press.

[3] M. Volpe, R. Inguanta, S. Piazza, C. Sunseri, Surf. Coat. Technol., 200, 5800 (2006).

[4] R. Inguanta, M. Amodeo, F. D’Agostino, M. Volpe, S. Piazza, C. Sunseri, J. Electrochem. Soc., in press.

# Electrochemical Deposition of Thin Polypyrrole Films on Silicon Substrates

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Conducting polymers offer a unique combination of properties, which are interesting for sensoric, microelectronic, and especially photovoltaic applications. [1-3]

Outstanding for this class of materials is the possibility to obtain these polymers in a metal-like conducting state or as semiconductors depending on the oxidation state of the polymer. Utilising this, it is possible to build up Schottky diodes or p-n junctions, respectively. [4,5]

The deposition of polypyrrole was vastly investigated by numerous scientists, [6] despite this, there are only few works on the electrochemical deposition of polypyrrole films on silicon substrates. [4,5]

Our investigations were focussed towards an enhanced electronic contact between silicon substrates and electrochemically deposited thin polypyrrole films. The passivation behaviour of silicon substrates with thin polypyrrole films compared to hydrogen-terminated silicon surfaces was also examined.

Polypyrrole films were deposited electrochemically out of aqueous solutions utilising different deposition procedures, including cyclic voltammetry, galvanostatic deposition, and multi-pulse electrochemical deposition.

The quality of the thin polypyrrole films was strongly dependent on the pH of the electrolytes and on the anions present in solution.

Characterisation of the thin polypyrrole films was conducted by infrared spectroscopic ellipsometry, Raman spectroscopy, and electrochemical methods.

[1] J.W. Schultze, H. Karabulut, Electrochim. Acta 50 (2005) 1739
[2] H. Spanggaard, F.C. Krebs, Sol. Energy Mater. 83 (2004) 125.
[3] N. Hall, H. Shirakawa, A. MacDiarmid, A. Heeger, Chem. Commun. (2003) 1.
[4] O. Inganäs, T. Skotheim, I. Lundström, Physica Scripta 25 (1982) 863.
[5] A. Watanabe, S. Murakami, K. Mori, Y. Kashiwaba, Macromol. 22 (1989) 4231.
[6] S. Sadki, P. Schottland, N. Brodie, G. Sabouraud, Chem. Soc. Rev. 29 (2000) 283.

# Adsorption kinetics of ATP anion on Bi(111) single crystal plane electrode

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This work is a part of the project devoted to the study of the influence of the chemical nature and crystallographic structure of the electrode surface on adsorption kinetics of the neutral biochemically active organic molecules and various organic cations and anions at the Bi | electrolyte interface [1-3]. Comparison of the results for the various organic compounds and organic ions demonstrates that the kinetic mechanism of adsorption depends noticeably on the nature of the metal as well as on the geometrical structure of adsorbed layer uracil adsorption is limited mainly by the heterogeneous adsorption step, but adsorption of D-ribose, adenosine as well as tetrabuthyl ammonium cations is limited mainly by the mixed kinetics at higher frequencies and by the diffusion step at lower frequencies.

Impedance spectroscopy has been employed for a quantitative study of ATP anion adsorption kinetics at the Bi(111) single crystal plane | 0.05M $Na_2SO_4$ + 0.005M $NaH_2PO_4$ + 0.005M $Na_2HPO_4$ aqueous base electrolyte (pH = 6.8) interface. Analysis of the impedance data demonstrates that the adsorption process of the ATP anion at high negative surface charge density is limited by the rate of the diffusion and heterogeneous adsorption steps of the organic anion to the electrode surface. In the region of maximal adsorption the slow diffusion stage seems to be the rate-determining step of adsorption in the case of dilute $ATP^{2-}$ solutions. For more concentrated solutions of $ATP^{2-}$ the 2D, 3D or hemimicelle formation processes are possible, indicating the so-called anomalous diffusion mechanism in the double i.e. adsorption layer region.

The non-linear regression analysis has been used for the fitting of the experimental Nyquist plots. In the potential region $-1.3 < E < -0.55$V (SCE), to a first approximation, the Frumkin – Melik-Gaikazyan equivalent circuit can be used for the simulation of $ATP^{2-}$ adsorption from dilute solutions. More complicated equivalent circuits have been tested for the simulation of experimental impedance data at $-1.7 < E < -1.3$V (SCE), where the electroreduction of the base electrolyte components is possible in addition to $ATP^{2-}$ desorption. The limiting double layer capacitance, adsorption capacitance and diffusion resistance depend on the electrode potential as well as on the adsorbate concentration. The characteristic time constant for $ATP^{2-}$ adsorption is lower than these obtained for D-ribose, adenosine and uracil.

## References

1. A. Jänes, K. Lust, E. Lust, J. Electroanal. Chem. 548 (2003) 27.
2. G. Nurk, H. Kasuk, K. Lust, A. Jänes, E. Lust, J. Electroanal. Chem. 553 (2003) 1.
3. H. Kasuk, G. Nurk, K. Lust, E. Lust, J. Electroanal. Chem. 550-551 (2003) 13.

# Mediated enzyme electrochemistry for biocatalytic fuel cells.

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Biocatalytic fuel cells present a realistic opportunity for provision of implantable power, given the exquisite selectivity of enzyme catalysts, their activity under physiological conditions, and the relative ease of immobilization of isolated enzymes. Electronic communication between electrode surfaces and biocatalysts in biocatalytic fuel cells can be achieved by direct electron transfer. Current and power densities achieved with electrodes using the direct electron transfer approach will be limited, however, because of the need to have intimate contact between the two-dimensional electrode surface and a coating monolayer of correctly oriented biocatalyst. The use of small redox molecules that can mediate electron transfer between the biocatalyst and the electrode surface offers an opportunity to improve output from biocatalytic electrodes, as three dimensional films of biocatalysts may now be used.

We are interested in development of a biofuel cell[1] consisting of a glucose oxidase-based anode and a laccase-based cathode using osmium-based redox complexes as electron transfer mediators.[2]

Here we present a synthetic strategy for the preparation of a library of redox mediators for biocatalytic fuel cells. These mediator are designed to possess the dual function of mediation and amenability to covalent immobilisation at electrode surfaces. This approach is aimed at improving the stability and the power output of the biofuel cell working in pseudo-physiological conditions.

1. A. Heller, *Phys. Chem. Chem. Phys.*, 2004, 6(2), 209
2. (a) F. Barrière, Y. Ferry, D. Rochefort, D. Leech, *Electrochem. Com.*, 2004, 6(3), 237. (b) F. Barrière, P. Kavanagh, D. Leech, *Electrochim. Acta* 2006 (51) 5187

# Carbon assisted heat-treatment for synthesis of $Li_4Ti_5O_{12}$ nanoparticles

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$Li_4Ti_5O_{12}$ is a potential anode material for Li-ion battery becuase it has good Li-ion insertion/deinsertion reversibility with negligible structure change during discharge-charge cycling. Recently, fabrication of nano-sized active materials become a hot topic torward high rate battery applications. The use of nano-sized $Li_4Ti_5O_{12}$ has been shown to improve the rate capability significantly. However, a high temperature sintering is always necessary to prepare pure and well-crystallized $Li_4Ti_5O_{12}$ phase, no matter in solid-state reaction process or in sol-gel process. So the fabrication of nano-sized $Li_4Ti_5O_{12}$, especially with good dispersivity, is rather difficult. In this work, we prepared homogeneous $Li_4Ti_5O_{12}$ nanoparticles of ca. 100nm using acetylene back (AB) carbon as sintering assistant. The as-prepared nanocrystalline $Li_4Ti_5O_{12}$ exhibits excellent lithium storage capacity, especially good high rate performance.

The precursors for synthesizing nanocrystalline $Li_4Ti_5O_{12}$ were prepared by sol-gel method from titanium tetraisopropoxide (TTIP) and lithium acetate dihydrate with or without using high specific surface area AB as sintering assistant. The powders were finally sintered at 750℃ for 2h to complete the phase transformation.

The sample without using AB sintering assistant shows tightly agglomerated particles of 1-2μm with primary crystallite size of ca. 100nm. By contrast, when using AB sintering assistant, well-divided $Li_4Ti_5O_{12}$ particles was obtained, indicating that AB has acted as a barrier to prevent the agglomeration of $Li_4Ti_5O_{12}$ grains during sintering. As shown in Fig. 1, at a low current density of 0.1 A/g, the pure sample shows a comparable capacity to the AB added sample, namely, 152 and 157 mAh/g, respectively. However, with increasing the current rate, the difference between the lithium storage capacities of these two samples becomes evident. The sample sintered with AB behaves a very slow capacity fading upon increasing the current density. 86% of the capacity cycled at 0.1 A/g can be maintained when being cycled at 1 A/g. However, the capacity of the densely agglomerated sample drops very rapidly, leaving only 30% of the capacity at 0.1 A/g when being cycled at 1 A/g. After 100 cycles at 1 A/g, the sample sintered with AB still delivers a charge capacity of 110 mAh/g, see Fig. 2, much higher than that of the reference sdample.

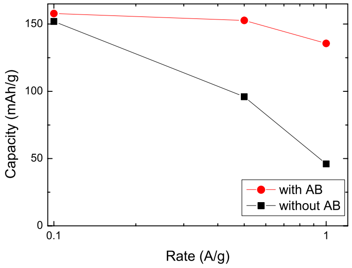

Fig.1. Rate-capabilities of the samples prepared with and without using AB sintering assistant in the sol-gel process.

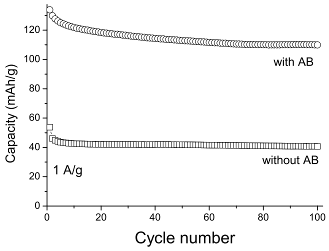

Fig.2. Cycle performance of the samples prepared with and without using AB sintering assistant at 1 A/g.

# Copper Nanostructured/ Modified $SnO_2$ Electrodes – Preparation, Surface Characterization and Electrochemical Behavior

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The electrocatalytic activity of nanostructured copper particles towards oxygen reduction is interesting due to the possible application in electrocatalysis and fuel cell. On the other hand, the electrocatalytic activity of nanostructured metal oxides for the electrochemical mineralization of organics is well known. In this work we present the preparation and characterization of modified $SnO_2$ electrodes on copper nanostructured support. This work is divided into three main parts:

- elaboration of the nanostructured Cu support;
- synthesis of modified $SnO_2$ nanoparticles surface characterization of the nanostructures;
- electrochemical characterization of the nanostructured Cu/$SnO_2$ electrodes;

The copper nanostructures were obtained by deposition through an alumina membrane (AAO) that is later dissolved. The diameter of the copper nanorods deposited on Cu is about 200 nanometres, which is in good agreement with the AAO membrane pore size used in the electrolysis process. The nanorods were found to be vertically aligned and no collapsing was observed with the height deposited, which was around 2 μm.

Tin dioxide was obtained by using hydrothermal synthesis. The obtained average particles size, observed by TEM, was 3 nm. The X-ray diffraction pattern showed that pure phase, tetragonal tin dioxide was obtained. The chemical surface modification of $SnO_2$ nanoparticles was done starting from a solution of $SnO_2$ particles in ethanol - phosphate ester - polyvinyl butyral a dispersant.

Electrochemical characterisation of nanostructured Cu/$SnO_2$ electrodes was performed with a BAS100W computer aided potentiostat, equipped with a three- electrode system (WE- nanostructured Cu/$SnO_2$; CE-Pt wire and RE-standard calomel electrode).

On nanostructured Cu/$SnO_2$ electrodes, the oxygen reduction occurs at – (0.6-0.65) V with an increase in the reduction peak current and decrease in overpotential when compared with copper nanorods. This result suggests that these structures can be used for catalytic oxygen reduction.

Further work is in progress to study the electrode reaction kinetics and the electrocatalytic activity of these electrodes for the total oxidation of phenols.

# Nanostructured Anode Oxides for Electrooxidation of Formaldehyde

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Electrooxidation, part of a domain of great interest electrocatalysis, is more and more intensely researched. The electrochemical methods of anodic oxidation for the treatment of waste waters containing organic polluting agents have drawn attention [1] mainly because of the easy control and high efficiency ensured by the use of new electrode materials [2]. Later, modified DSA type electrodes incorporation Sn, Sb and Ir have been used for the oxidation of some organics pollutants [3]

The formaldehyde, a small pollutant molecule can be considered as model molecule.

Three different oxide electrode $SnO_2$/Ti, Sb/$SnO_2$/Ti, $SnO_2$/$IrO_2$/Ti obtained by sol-gel procedure. Voltammetric experiments were performed in a classical three electrodes cell, where the WE was the mentioned anodes and for electrolysis the micro-flow cell (Electrocell) was used.

For the composition $SnO_2$/$IrO_2$/Ti the deplacement for the more positive value in the presence of formaldehyde is higher.

During the electrolysis in galvanostatic conditions (i=20-60 $mAcm^{-2}$) the decrease of formaldehyde concentration and the oxidation products (formic acid and carbon dioxide) have been followed. The oxidation is a function of anode nature, electrolysis time and conditions. After 4 hours of electrolysis the decrease of formaldehyde concentration was higher for the anode containing Ir (96-98%). The concentration of the initial formed formic acid is higher after 2-2.5 hours, when the $CO_2$ concentration (calculated from mass balance) is more important. That is experimental evidence for the formation of $CO_2$ from formic acid.

Further work is in progress to improve the electrocatalytic properties of $SnO_2$/$IrO_2$/Ti electrodes by changing the rapports Sn/Ir and the experimental parameters for their preparation. The electrodes will be tested concerning the electrocatalytic activity for the oxidation of other pollutants.

References

1. P.Tissot, M.Fragniere, J.Appl.Electrochem. 24 (1994) 509-512
2. C.H. Comninellis, G.P. Vercesi, J.Appl.Electrochem. 21 (1991) 335-345
3. R.Ferrigno, C.H. Comninellis, V.reid, C.Modes, R.Scanell, H.H. Girault, Electrochim.Acta 44 (1999) 2871.

# Molecule and Ion Transport inside of Carbon Nanotubes

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Ion and molecule transport in nanoscale channels have recently received increasing attention. It was shown that nanoporous channels like carbon nanotubes (CNT) have opened new applications as storage materials and fluid flow channels with high capacity and stability.

An important role in electrochemical storage devices is played by non-aqueous electrolyte solutions confined by CNT. Unfortunately, direct experimental investigation of non-aqueous electrolyte solutions inside carbon nanotubes meets essential problems.

Thereby in the present work we have performed molecular dynamics simulations of several ions dissolved in acetonitrile (AN) confined by single-walled armchair carbon nanotubes of different diameter by using the author's programme package MDCNT [1]. Structure of pure solvent and ionic solutions was studied in terms of radial distribution functions, running coordination numbers and different kinds of specific 3D and orientational space-correlation functions. It was shown that carbon nanotube greatly reinforces liquid structure, and this effect is always influenced by carbon pore diameter.

Dynamic properties of AN molecules and dissolved ions were analyzed using a wide set of time-correlation functions, relaxation times, diffusion coefficients, etc. Ion migration through carbon nanotubes was also measured. The dependence of ionic transport on nanopore diameter was found. It was determined that transport properties of electrolyte solutions based on AN confined by CNT differ from bulk properties only if the diameter of CNT is less then 4-5 nm.

## Acknowledgements

This work was partially supported by Ukrainian-American Laboratory on Computational Chemistry, Kharkiv, Ukraine, Jackson, MS, USA (project «Structure and Dynamics in Electrolyte Solutions confined by Carbon Nanotubes»).

## References

1. Oleg N. Kalugin, Vitaly V. Chaban, Yaroslav V. Kolesnik. *Molecular dynamics simulation of liquid acenotitrile and solution of $Li^+$ in it inside of carbon nanotubes by using MDCNT package.* Kharkiv University Bulletin. 2006. No 597. Chemical Series. Issue 11 (34).

# Photoelectrochemical properties of GaN nanodots

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Over the last few decades, a considerable number of studies have been reported on hydrogen generation from water using oxide semiconductor electrodes such as titanium dioxide. Nitride semiconductor is another candidate for water splitting because GaN is stable in chemical solutions and its band-edge potentials are suitable for water splitting. Very recently, hydrogen generation using GaN as electrodes has been reported [1] however with lower energy conversion efficiency. In order to enhance the energy conversion efficiency, the surface area of the electrode should be increased. In this report, we propose GaN nanodots as a new photoelectrode for hydrogen generation.

GaN nanodots, formed on n-type Si(111) by plasma assisted molecular beam epitaxy (P-MBE) under N-rich conditions [2], were used as a working electrode. After removing impurities from as grown wafer by etching in 1.0 mol/L HCl for 24 hr, photoelectrochemical measurements were performed in 1.0 mol/L HCl aqueous solution (pH = 0.1). The measurements were carried out with a Pt counterelectrode and a 500 W xenon lamp for illumination if needed.

A typical scanning electron microscope (SEM) image of as grown surface is shown in Fig. 1. GaN nanodots were successfully formed on Si surfaces. Figure 2 shows current density-voltage characteristics of a GaN nanodot specimen under illumination and in the dark compared with those of n-type Si. The n-type Si shows quite low photocurrent density. An enhancement in current density of a GaN nanodot specimen under illumination compared in the dark is clearly observed. These observations indicate that GaN nanodots are very promissing as a photoelectrode for water splitting.

[1] K.Fujii, T.Karasawa, and K.Ohkawa, Jpn. J. Appl. Phys. 44 (2005) L543.
[2] M.A. Sánchez-García *et al.*, J. Cryst. Growth 183 (1998) 23.

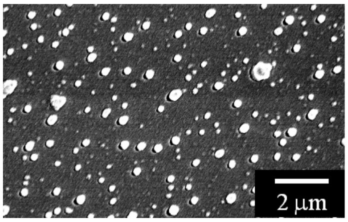

Fig.1. SEM image of GaN nanodots.

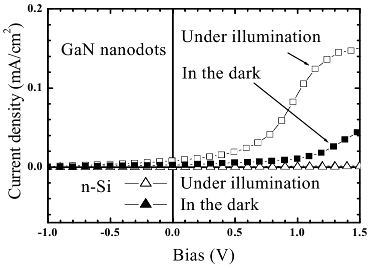

Fig.2. Current density-voltage curves of GaN nanodots and n-type Si.

# Enhancement of Rate Capability of Layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ Materials for Li Secondary Batteries

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A lithium cobalt dioxide has been used as an active material in a commercial lithium secondary batteries, since it shows excellent electrochemical performances as well as easy preparation. However, there are some demerits such as relatively low practical capacity, high cost, toxic, and low thermal stability. Recently, new cathode materials such as $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.5}Co_{0.5}$, $LiNi_{0.5}Mn_{1.5}O_4$, and $LiNi_xCo_{1-2x}Mn_xO_2$, which are obtained from substituting electrochemically active element (Ni, Mn) for Co, have been received attention, because they show high discharge capacity, thermal stability, and cycle performance.

In this study, surface of a layered $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ material was coated with a carbon to enhance rate capability and thermal stability, and its electrochemical and thermal performance was evaluated.

The electrodes were fabricated from 86: 6: 8 (mass%) mixture of active material: polyvinylidene difluoride (PVDF, Aldrich) as binder: Super-P carbon black (MMM Carbon) as current conductor. The PVDF was dissolved in N-methylpyrrolidinone (NMP, Kanto) and the active material and conductor mixture were added. The slurry was then coated on a thin aluminum foil (20 µm thick) and dried overnight at 120 ºC. The electrochemical cells were prepared in standard 2016 coin cell hardware with lithium metal foil used as both the counter and reference electrodes. Cells were assembled in a dry room (dew point was below -55 ºC). The electrolyte used for analysis was 1.15 M $LiPF_6$ in ethylene carbonate/ diethyl carbonate (EC/DEC, 1/1). The cells were taken out of the dry room and placed on the battery testing system (Toscat 3000). Rate capability of the coated materials was evaluated at, various discharge currents such as 0.2C, 0.5C, 1C, 2C, 5C, 10C, and 20C rate. The charge and discharge cycling tests of the cells were conducted galvanostatically at a 0.5C rate in a voltage range of 4.3 to 2.8 V. Thermal stability of the materials was measured using DSC (differential scanning calorimetry). The sample was dried at 80 ºC for 24 h after charging at 4.3 V. The measurements were carried out using a DSC Q1000 at a temperature scan rate of 10 $^{\circ}C\,min^{-1}$ in a nitrogen atmosphere.

Capacity values from the material without the carbon coating are 151.4mAh/g for 0.2C and 112.8mAh/g for 5C. The charge retention rate of 5C/0.2C was 84.5%. The 1% carbon-coated material gave 153.4 mAh/g for 0.2C, 132.0mAh/g for 5C, and the retention rate of 86.1%. Also, the 3% carbon-coated material gave 136.8mAh/g and 90.0% charge retention. Carbon coatings might improve the electronic conductivity of the active material, which induced the better rate capabilities of the carbon-coated material.

# Electrochemical Studies of Unit Cell for IT-SOFC

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Solid oxide fuel cell (SOFC) is an electrochemical conversion system with high efficiency and low-emission of pollution. The SOFC system with high performance and long-term stability is required to reduce the conventional operation temperature of 1000℃ to under 800℃ without penalty for the power density. Power density of unit cell can be decreased by the increase of the ionic resistance of the electrolyte at low temperature. Unit cell with anode supported-electrolyte was successfully prepared using tape casting method and the fabrication of SOFC unit cell with thin film electrolyte was made by tape casting process in which the thickness of electrolyte could be more thinner (about 10μm). Cathode layer was formed on the anode-supported electrolyte of 10μm thin film by screen printer. Thin electrolyte layer was successfully fabricated for two unit cell and the active layer in anode was also successfully formed. It was confirmed that both anode layer and cathode layer were well adhered to the YSZ layer of electrolyte by SEM micrographs. The YSZ layer of electrolyte for the anode with double layer shows porosity-free and quite dense as compared with anode and cathode layer. As a result of porosity measurement, both layers for anode and cathode showed a good porosity needed for gas diffusion, namely 33% for anode and 27% for cathode. The I-V characteristics of unit cell with active layer of at 700-800 ℃ and the maximum power densities of unit cell at 800 ℃, 750 ℃ and 700 ℃ were 0.23 W/cm$^2$, 0.18 W/cm$^2$, and 0.13 W/cm$^2$, respectively. The impedance spectra of Sample B were also measured at 700 ℃ and 800 ℃. The interfacial polarization resistance at 800℃ was considerably reduced as compared with the result of 700 ℃ while the electrolyte resistance was negligible at 700 ℃ and 800℃. This result revealed that further improvement of electrode activity for anode-supported electrolyte unit cell was very necessary in the next study.

# Redox properties of Colloidal CdTe Quantum Dots

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The relative position of the energy bands in quantum dots (q-dots) is determined by (i) the size of the nanocrystalline domains and (ii) the effect of adsorbed species (protecting shell) on the electron density. Although the former contribution can be obtained from sophisticated modelling of the electronic structure [1], the contribution from the protecting group requires detailed information on the surface composition of the dots. In the present communication, the position of the band edges of colloidal CdTe q-dots protected by 3-mercaptopropionic acid (MPA) is investigated in aqueous solution employing a rotating disc electrode and UV-Visible spectroscopy.

Water-soluble CdTe q-dots protected by 3-mercaptopropionic acid (MPA) were synthesised using a two-step synthesis protocol [2], yielding average core radii in the range of 1.70 to 2.44 nm. The onset potential for hole-injection into the q-dots was measured employing a carbon rotating disk electrode. Detailed analysis of the current-voltage behaviour as a function of the electrode rotation rate provided information on the position of the valence band edge. Size independent features were associated with ligand induced surface states in the dots. Finally, dynamic aspects of the hole-injection into the q-dots were extracted from Koutecký-Levich plots. At potentials more positive than that of the valence band edge, the injection of up to several hundreds of holes into a single dot was estimated.

[1] A.L. Efros and M. Rosen, Phys. Rev. B 58 (1998) 7120.
[2] H. Zhang and B. Yang, Thin Solid Films 418 (2002) 169.

# Interactions between phosphorus dendrimers and heparin

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Dendrimers have recently gained a considerable interest. These nanostructures have been used in many fields, especially intensively in biomedicine. Although all dendrimers share the same globular structure with plenty of surface groups on the surface and empty internal cavities, their specific properties depend on a chemical composition. Our studies focused on cationic phosphorus dendrimers [1]. We observed that these dendrimers formed association structures with heparin. Such complexes may be of interest in the oral delivery of heparin or as antiangiogenic compounds. Interactions with heparin were previously found for several types of dendrimers [2, 3]. However, according to our observations only phosphorus dendrimers created very regular structures with heparin, contrary to other dendrimers such as polyamidoamine dendrimers or polypropyleneimine dendrimers. The regularity of these assemblies was confirmed by experiments with a fluorescent dye thioflavine T (ThT). During a spectrofluorimetric titration of heparin/ThT solution with dendrimers an increase of ThT fluorescence intensity followed by a plateau was observed. ThT is a popular probe to study the formation of amyloid aggregates since its fluorescence selectively depends on steric constraints of ThT rings rotation. Upon excitation an intramolecular charge transfer between ThT rings occurs. This charge shift can be stabilized if one of the rings rotates by $90^{o}$, then the reverse charge is impossible [4]. This condition is met when ThT binds to the fibrils with its long axis parallel to that of the fibrils [5] and does not occur when ThT is in the presence of amorphous protein aggregates. Fibrils are the most regular naturally occurring protein aggregates. It allows for conclusion that the phosphorus dendrimers and heparin must create a kind of a net that incorporates ThT molecules in a similar way as fibrils do.

[1] Majoral., J. P., Caminade, A. M., Laurent, R. & Sutra, P. (2002) Phosphorus-containing dendrimers: From material science to biology. Heteroatom Chem. 13, 474-485
[2] Kasai, S., Nagasawa, H., Shimamura, M., Uto, Y. & Hori, H. (2002) Design and synthesis of antiangiogenic/heparin-binding arginine dendrimer mimicking the surface of endostatin. Bioorg. Med. Chem. Lett. 12, 951-954
[3] Imae, T., Hirota, T., Funayama, K., Aoi, K. & Okada, M. (2003) Binding of poly(amido amine) dendrimer to sodium hyaluronate in aqueous NaCl solution. J. Colloid Interface Sci. 263, 306-311
[4] Voropai, E. S., Samtsov, M. P., Kaplevskii, K. N., Maskevich, A. A., Stepuro, V. I., Povarova, O. I., Kuznetsova, J. M., Turoverov, K. K., Fink, A. L. & Uverskii, V. N. (2003) Spectral properties of thioflavin T and its complexes with amyloid fibrils. J. Appl. Spectrosc. 70, 868-874
[5] Krebs, M. R. H., Bromley, E. H. C. & Donald, A. M. (2005) The binding of thioflavin T to amyloid fibrils: localisation and implications. J. Struct. Biol. 149, 30-37

# Pore-Spanning Bilayer Lipid Membranes

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Investigations on the formation of pore-spanning bilayer lipid membranes (psBLMs) with the prospect of functional reconstitution of transmembrane proteins were undergone. For reference purposes, classical free-standing BLMs were prepared by painting over apertures either in a PTFE foil or a microscope cover glass chip. To preserve the benefits of classical BLMs and subdue their shortcomings, attempts were made to form psBLMs by ways other than painting. For this purpose, a variety of substrates was explored. Multiporous substrates with pore diameters in the 100 nm range (silicon nitride thin films on gold, aluminum oxide membranes) and substrates bearing single pores of ~2 µm (microscope cover glass) or several tens of nanometers (free-standing silicon nitride membranes) were investigated. Emphasis was put on psBLM formation via spreading of giant unilamellar lipid vesicles (GUVs). Fluorescence microscopy was employed to monitor vesicle spreading and planar lipid bilayer formation over substrates. GUVs were observed to sink to a horizontally mounted substrate and remain intact at low salt concentrations. Upon increase of salt concentration or introduction of specific ionic species spreading of GUVs at the substrate-electrolyte interface was induced. Isolated planar lipid bilayer patches were formed that were able to fuse with neighboring patches to form larger domains. psBLMs were probed by means of time and frequency-resolved AC impedance spectroscopy. The best results were obtained on silicon-based substrates with pores confined to a specific area.

# Discharge Characteristics of Polypyrrole/Silver Vanadium Oxide Composite Used for Lithium Primary Batteries

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Silver vanadium oxide (SVO), $Ag_2V_4O_{11}$, is the cathode of choice in lithium primary batteries for implantable cardioverter defibrillators (ICDs) owing to its high gravimetric/volumetric energy densities [1]. Seven moles of lithium can be theoretically inserted into SVO, yielding a discharge capacity of ca. 315 mAh $g^{-1}$; however, much lower utilization of SVO is practically attained, especially during pulse discharges with high rates. The internal cell resistance drastically increases with progressing discharge, resulting in a poor rate-capability of a Li/SVO cell.

In this work, an SVO electrode was coated with a conducting organic polymer, polypyrrole (PPy), in order to improve the electrochemical performance of SVO. A hybrid composite of PPy/SVO was synthesized by an oxidative polymerization of pyrrole monomer on the SVO surface in an acidic medium [2]. Galvanostatic discharge experiments showed that the composite electrodes with 7.0 – 12.5 wt% PPy exhibit higher discharge capacity as compared with the pristine SVO electrode. Also, the pulse discharge experiments performed under battery operation conditions inside an ICD showed an improved power capability of the composite electrode.

The ac-impedance study indicated that the improvement in electrochemical performance of the composite electrode is attributed to PPy which facilitates the interfacial charge transfer kinetics by forming an effective conductive network on the SVO surface and thus enhances the SVO utilization.

References

[1] K.J. Takeuchi, A.C. Marschilok, S.M. Davis, R.A. Leising, E.S. Takeuchi, Coordin. Chem. Rev. 219-221 (2001) 283.
[2] J.-W. Lee, B.N. Popov, J. Power Sources 161 (2006) 565.

# Composite galvanic coatings with ceramic nanoparticles for industrial applications: the cases of copper, nickel, bronze on metallic substrates

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Nanoscaled materials characteristics differ from bulk materials and from micro sized powders. The higher surface area affect their chemical and physical properties, allowing the design of new materials with improved optical, thermal, mechanical, chemical, electrical performances.
In the last years, the progress in the synthesis of nano- scaled materials promoted the use of nano- crystals in many different fields, for instance in optoelectronics, biomedical, energy conversion and photocatalysis. In particular, the production of composite galvanic coatings reinforced with the addition of SiC nanopowders was studied first in laboratory scale dealing with nickel deposits on steel. The study of corrosion behaviour, as well as of physical properties of these composite coatings led us to widen the research to Cu-nanoSiC codeposits, which were compared with pure copper deposits obtained under pulsed current, as well as on bronze-nano SiC deposits. The results were so satisfactory that we could afford the higher scale application on objects of industrial interests.

The present work will deal with the discussion of some results obtained on:
Propellers for military vessels coated with Ni-SiC composite deposit
Carbon steel railways wagons axes with the same kind of deposit
Brass pasta extruders coated with lead-free bronze-SiC nano deposits and copper – SiC micro composite deposit

# Nanostructures Prepared via Electrodeposition at a Liquid-Liquid Interface

## Controlled Synthesis and Physical Properties Investigation of Metal/Polymer Nanocomposites

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The controlled tailoring of new functional materials has been of interest of many research groups nowadays. Special attention is brought to a synthesis of metal colloids coated with polymer. As a metal element, gold has been of interest due to its electronic and catalytic properties. It has been previously shown that for generating such metal nanocomposites, an electrochemical synthesis carried out at an interface between two immiscible solutions represents a suitable method.[1,2]

A gold – polymer nanostructures have been prepared via electrodeposition at water/1,2-dichloroethane interface at various experimental conditions. The obtained results show that nanoparticles of different sizes can be synthesized by an electrochemical system modification. The stability of the prepared nanostructures has been confirmed.

The electrochemical process is studied by cyclic voltammetry measurements using a four-electrode electrochemical cell. The kinetic parameters are calculated using both Nicholson method and Butler-Volmer formation, and the results are analyzed in relation to the material structure.

To obtain physical properties of the generated nano-sized material, different analytical techniques have been employed. Transmission electron microscopy is used to describe the material structure and to monitor the growth of gold particles in the polymer matrix. UV-Vis spectroscopy and X-ray photoelectron spectroscopy are used to generate additional structural parameters of the studied matrix.

References:

[1] M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Comm. 7 (1994) 801.
[2] R. Knake, A. W. Fahmi, S. A. M. Tofail, J. Clohessy, M. Mihov, V. J. Cunnane, Langmuir 21 (2005) 1001.

# Electrosynthesis of Bilayer Coatings Based on Azulene and Prussian Blue

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Azulene is a non-alternate hydrocarbon, consisted of an unsaturated seven member ring fused with an unsaturated five member ring. Azulene derivatives can be deposited onto electrode surfaces as thin conjugated polymeric films that exhibit specific electronic and optical properties. Prussian Blue (PB), ferric ferrocyanide, has been extensively studied owing to its electrochromic and electrocatalytic properties. In the present work, new azulene derivatives such as 2-(2-azulene-1-yl-vynil) thiophene, 3-(2-azulene-1-yl-vynil) thiophene, 3-[(E)-2-thiene-2-yl-vynil] azulene-1-carboxilic acid and 3-[(E)-2-thiene-3-yl-vynil] azulene-1-carboxilic acid were investigated. The bilayer films have been prepared by a two-step method. Firstly, the azulene polymer (PAz) has been electrogenerated onto platinum electrode surface. Subsequently, the modified electrode has been covered by Prussian Blue film deposited on top of Pt/Paz electrode. The Pt/Paz/PB modified electrode was investigated both in aqueous and non-aqueous solutions by using cyclic voltammetry.

# First Principles Study on a Single Molecular Diode

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Since the first theoretical demonstration by Ratner and Aviram [1] that an organic molecule could function as a molecular diode, the idea of using organic molecules as functional units in electronic devices has received great attention [2]. Among those molecular electronic devices, diodes are one of the most commonly used electronic devices in the circuit. The basic idea to make a molecular diode is to introduce asymmetry in the structure of the molecule. In the present study, we considered a molecular rod with a donor and an acceptor unit that was designed to act as a diode when wired into the circuit as shown in the inset of Figure a. The nonequilibrium Green' function technique combined with density functional theory was used to perform *ab initio* quantum-mechanical calculations of the electronic transport properties of the molecule. The results demonstrated the rectification behaviour of the molecule, which is consistent with the experimental results by Elbing *et al* [3]. The asymmetric evolutions of the energy levels and spatial distributions of the frontier molecular orbitals with the applied voltage are found to be essential in generating this molecular rectification.

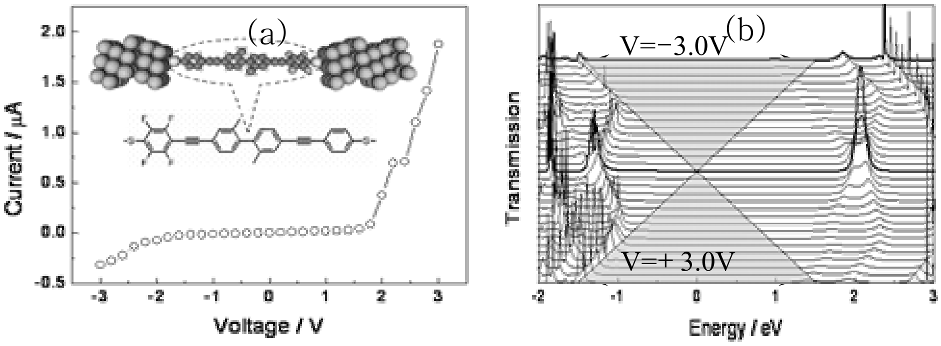

Figure 1. (a) The calculated current-voltage curve of the system under study. Inset: schematic structure of the molecular junction. (b) The transmission spectra of the molecule at different voltages (each curve is vertically shifted for clarity, representing a difference of 0.2 V and the thick black line represents the transmission spectrum at equilibrium; the grey region is the *bias window*).

References
[1] A. Aviram, M.A. Ratner, Chem. Phys. Lett. 29 (1974) 277.
[2] C. Joachim, J.K. Gimzewski, A. Aviram, Nature 408 (2000) 541.
[3] M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C.V. Hanisch, F. Weigend, F. Evers, H.B. Weber, M. Mayor, PNAS, 102 (2005) 8815.

# Electrochemical Constructions of the Nano-Micro Structured CaP Coatings on Titanium and Its Interaction with Protein

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We have successfully constructed a novel nano-micro structured calcium phosphate (CaP) composite coatings, including octacalcium phosphate (OCP) and hydroxyapatite (HAp) on titanium by using an electrochemical deposition technique. The physico-chemical and biological properties of the coating were characterized by SEM, XRD, FT-IR, Raman and *in vitro* cell culture and in vivo test respectively. It is suggested that under controlled deposition conditions, the primary CaP nanowires grow and self-assemble to construct an ordered micro-porous nest-like morphology, thus to form a nano-micro two-level structure. The CaP nanowires are orderly arranged with their c-axis preferentially perpendicular to the substrate surface. It is demonstrated that the CaP composite coatings exhibit a preferable biocompatibility, because they are similar to the natural bone in structure. An in situ ATR-FTIR study of bovine serum albumin (BSA) adsorption on HAp has been carried out in this work. The adsorption process of BSA onto HAp surface can be considered as in two different steps. The first step is fast and results a direct adsorption of BSA to HAp surface. The second step may last for several hours, more protein adsorbs on the surface in this process, and the structure of protein changes with time due to the interaction between protein and biomaterials. The in situ measurements of quartz crystal microbalance (QCM) indicate that $Ca^{2+}$ play an essential role in the protein absorption on the HA surface because of negative charge for BSA. It is found that, when reacting with BSA, the phosphate band of HAp in solution shifts to higher wavenumbers, indicating that $PO4^{3-}$ can also be an adsorption site. The in situ study on the interaction between HAp and protein is helpful for further understanding of the bioproperties of nano biomaterials in molecule level.

# Sugar Sensing electrode based on PANI/$NiO_x$ composite

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Polyaniline (PANI) can provide a 3D network for incorporation of inorganic salts to provide enhanced electro-catalytic properties. A sugar sensing electrode was constructed by electrochemically depositing polyaniline in the presence of nickel salts. We have previously studied the electropolymerization of aniline in aqueous solutions of pH 2 to 12 and successfully obtained electroactive PANI from the whole pH range.[1] PANI-Nickel oxide ($NiO_x$) composite film was therefore electrodeposited for the first time from aniline and $NiSO_4$ in neutral solution through potential cycling between – 0.3 and 0.9 V *vs*. SCE. A characteristic IR spectrum of the composite is shown in Figure 1. The PANI/$NiO_x$ composite exhibited catalytic properties towards electrooxidation of polyhydroxyl organic compounds such as sugars.

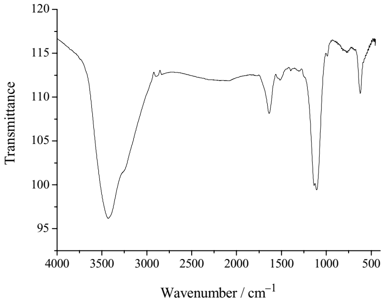

Fig. 1 FT-IR pectrum of PANI / NiOx composite film.

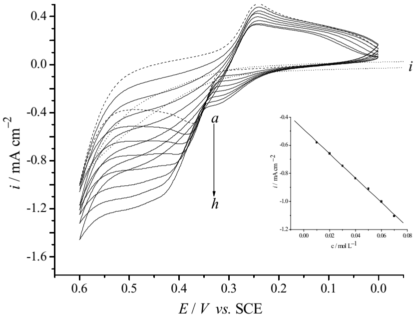

Fig. 2 Cyclic voltammograms of PANI / NiOx composite film with 10 to 70 mM glucose. Inset is a calibration curve obtained from the CVs.

Sensing electrodes constructed based on the composite film was evaluated for glucose and fructose measurement. At an overpotential of 0.46 V the sensor exhibited a linear concentration dependence on glucose from 1.0 to 70 mM (Fig. 2, $R = 0.9998$) and 10 to 100 mM for fructose ($R = 0.9935$) respectively. When a control sensor constructed with just $NiO_x$ and without Pani, the performance was inferior to the proposed sensor by resulting in much narrower detection ranges (0.1 to 10 mM for glucose and 0.1 to 30 mM for fructose). This may be due to inefficient electron transfer in the absence of PANI and hence much lower anodic current was observed.

## Reference

1. X.-X. Liu, L. Zhang, Y.-B. Li, L.-J. Bian, Z. Su, L.-J. Zhang, J Mater Sci. 40 (2005) 4511.

# Assemblies of dendrimers and proteins on electrodes for biosensing applications

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Electron transfer between a protein and an electrode surface can be considered as a mimetic process of the electron transfer through redox molecules chains in biological systems. A situation very close to in vivo conditions can be attained by building up ultrathin enzymes or proteins layers onto the electrode surface. Proteic materials are supposed to be organized in such a way that high enzymatic specificity and hence activity are reached. This can be achieved using layer-by-layer (LBL) self assembly of oppositely charged layers, a process which looks very much like the physiological recognition of redox partners before electron transfer, mainly based on electrostatic interactions.

Dendrimers are promising candidates for such functional coatings. They constitute a unique class of materials with a cascade, tree-like architecture, having well-defined geometrical sizes and surface functionality. They possess a unique surface of multiple chain ends and the number of surface groups can be precisely controlled as a function of synthetic generation. Interestingly, dendrimers of adjacent generations bear oppositely charged surfaces at controlled pH, depending on the nature of carboxylic or amine surface groups, thus opening the way for techniques based on electrostatic self-assemblies. The multilayered configuration based on dendrimers offers advantages for several applications including catalysis, encapsulation and controlled release, chemical and biological sensors, and biomimetic materials. Because of the interior void structure of dendrimers, the resulting multilayer film puts up only minimal diffusion restriction for analytes and electron-transferring substances ensuring desired enzymatic and electrocatalytic reaction over the whole range of multilayers.

We report in this paper results on fabrication of self-assembled composite multilayer films built from dendrimers of adjacent generations (G3.5 and G4) and from G3.5 or G4 dendrimers and polyions or proteins. Electrochemistry, Surface Plasma Resonance (SPR) and quartz crystal microgravimetry (QCM) have been used for investigating the microstructure and morphology of dendrimer/polymer or protein hetero-assemblies. We report on the possibility of constructing dendrimer/enzyme multilayers on electrode surfaces for use as a biosensing interface. Mixed protein/dendrimer assemblies have been constructed with proteins differing in charge, nature of the prosthetic groups and sizes such as lysozyme, mitochondrial cytochrome c, glucose oxydase or bacterial polyhemic cytochrome $c_3$. Glucose detection and metal bioremediation are particularly explored based on the preparation of multilayer films using G4 PAMAM or G3.5 PAMAM dendrimers, and redox proteins and enzymes such as glucose oxidase or bacterial polyhemic cytochrome $c_3$.

# Photoelectrochemical and photocatalytic properties of nanocrystalline $TiO_2$ electrodes

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The photocatalytic properties of $TiO_2$ for organic compound degradation have been widely studied. Under UV irradiation, electron and hole pairs are generated and can react with compounds adsorbed onto the $TiO_2$ surface [1]. Usually, the investigations are performed for $TiO_2$ suspensions. However, the exigency for separating the catalyst particles hindered its industrial application. Motivated to improve the efficiency and applicability of $TiO_2$ as photocatalyst, we are investigating nanocrystalline $TiO_2$ electrodes for application in electroassisted photocatalysis for water purification.

The electrodes were prepared by depositing a film of nanocrystalline $TiO_2$ particles (diameter of ca. 25 nm) from an aqueous suspension containing polyethylene glycol onto a transparent electrode, glass-FTO (fluorine-doped $SnO_2$), followed by heating at 450 $^{o}$C for 30 min. The resulting films, ca. 4 µm thick, were transparent and mechanically stable. SEM analysis revealed a very uniform and porous surface.

The electrochemical properties of the electrodes were investigated in aqueous solutions containing 0.1 M $Na_2SO_4$ as supporting electrolyte, Pt counter-electrode and Ag/AgCl as reference electrode. In the dark, the cyclic voltammogram exhibited a wide potential window, limited at –0,2 and +1,3 V due to $H_2$ and $O_2$ evolution. Defined peaks were observed for the electron transfer reaction of ferri/ferrocyanide redox couple; however, this redox system was not reversible at the nanocrystalline $TiO_2$ electrode, which exhibited a typical n-type semiconductor electrode behavior. Moreover, the electrochemical response of the $TiO_2$ electrode varied as a function of light intensity. The open circuit potential in aqueous 0.1 M $Na_2SO_4$, which corresponded to 0.15 V in the dark, changed to –0.26 V under 100 mW $cm^{-2}$ of polychromatic irradiation.

The catalytic activity of the $TiO_2$ electrodes was investigated for phenol (40 ppm) in 0,1 M $Na_2SO_4$ aqueous solution. In the dark, when the $TiO_2$ electrode was used as anode with application of an external potential of +1.1 V (which corresponded to the onset for phenol oxidation), a current of 3-5 $\mu Acm^{-2}$ was observed. After 3 h, determination of total organic carbon (TOC) in the solution revealed that the extent of phenol mineralization was 5 %. In heterogeneous photocatalysis configuration, when no external potential was applied, the irradiation for 3 h generated 25 $\mu Acm^{-2}$ of current and resulted in phenol degradation of 12 %. When the electrode was irradiated and used as anode with application of + 0,6 V, the generated current was 50 $\mu Acm^{-2}$ and the extent of phenol mineralization was 24 %. Thus, the nanocrystalline $TiO_2$ electrode exhibited a better efficiency for phenol degradation in the configuration of electroassisted photocatalysis. The application of the external potential can minimize electron and hole recombination, which is the major limiting factor for the efficiency of photodegradation process.

*Acknowledgments*. Fapesp, CNPq, W.F.Jardim, M.-A De Paoli, A.F. Nogueira.

[1] M.S. Hoffmann, S.T Martin, W .Choi, D.W Bahnemann, *Chem. Rev.* ***95*** (1995) 69.

# Dimethyl Ether Electro-Oxidation With Interdigitated Microarray Electrodes

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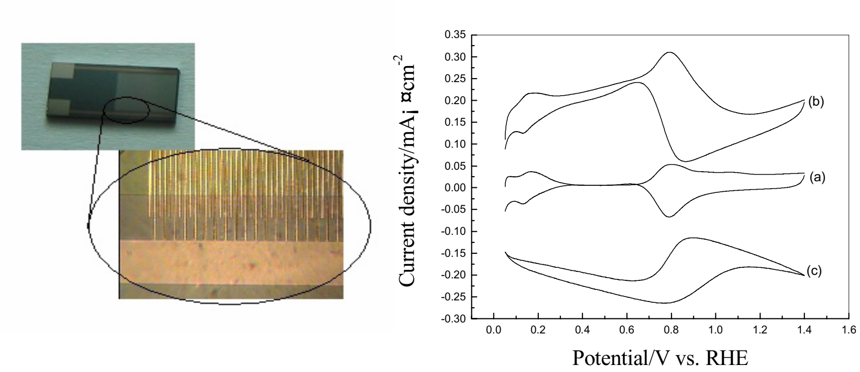
Abstract: The mechanism of dimethyl ether electro-oxidation [3,4] has been investigated by the interdigitated microarray (IDA) electrodes [1,2]. Cyclic voltammetry (CV) measurements have been performed on dimethyl ether in 0.5 mol/L sulfuric acid solution by different work style of IDA electrodes. A reduction current of $H^+$ corresponding to the adsorption and electro-oxidation of dimethyl at the generator electrode was detected at the collector electrode. In addition, the current densities of both the generator electrode and the collector electrode were influenced by the potential of the collector electrode. The adsorption of dimethyl ether will be weakened because of the attack of $H^+$.



Left: Metallurgical microscopy image of IDA electrodes. Right: Cyclic voltammograms of DME electro-oxidation on IDA electrodes in 0.5 mol/L $H_2SO_4$: (a) CV curve without the collector electrode. (b) and (c) CV curves of the generator and collector electrode, respectively, with the generator electrode scanning and the collector electrode under 0.02V vs. RHE.

References:

[1] K. Hayashi, Y. Iwasaki, R. Kurita, K. Sunagawa, O. Niwa. Electrochem. Commun., 5 (2003) 1037.
[2] P.R.M. Sila, M.A. El Khakani, M. Chaker, A. Dufresne, F. Courchesne. Sensors, Actuators B, 76 (2001) 250.
[3] J.T. Müller, P.M. Urban, W.F. Hölderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, J. Electrochem. Soc. 147 (2000) 4058.
[4] M.M. Mench, H.M Chance, C.Y Wang. J. Electrochem. Soc., 151 (2004) A144.

# Electrchemical Preparation and Characterization of Hybdrid Inorganic-Organic Materials for Electrochemical Sensing

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Electrochemical preparation and characterization of hybrid inorganic-organic films consisting of iron (III) hexacyanoferrate, well known as Prussian Blue (PB), and of organic conducting polymers, on a platinum electrode, are reported. The organic conducting polymers poly-[3,4-ethylenedioxythiophene] (PEDOT) and poly-[3-methylthiophene] (PMT) have been used for the preparation of hybrid films in various configurations, such as PB/PEDOT, PEDOT/PB and PMT/PB. The PB/PEDOT coating is prepared electrochemically by a two-step method. Firstly, a PB layer is electrodeposited onto a platinum electrode in aqueous solution. In the second step, the electrochemical deposition of PEDOT film over the Pt/PB modified electrode was carried out. The PEDOT/PB and PMT/PB coatings have been prepared in a similar manner, that is an inner layer of organic conducting polymer is firstly deposited onto platinum electrode surface and then the PB electrodeposition is carried out by potentiostatic and potentiodynamic procedure, respectively. Thereafter, the electrochemical behaviour and the stability of the hybrid coatings were studied in aqueous solutions. Whilst the electrochemical response of PB/PEDOT coating is based mainly on the Prussian Blue/Everitt Salt redox wave, the PEDOT/PB coverage shows no redox waves in the potential range from -0.5 to +0.5 V vs. ECS. On the contrary, the PMT/PB coating shows only the redox wave corresponding to the Prussian Blue/Everitt Salt system, which suggests that the PMT layer allows incorporation of PB near the electrode substrate surface. The electrochemical responses of these hybrid coatings demonstrate that (i) PB is able to conduct electrons through the outer organic polymer layer and (ii) potassium cation transport to the PB it is not impeded by the presence of the outer layer. This behaviour have been exploited in the electrooxidation of ascorbic acid at hybrid inorganic-organic coating modified electrodes, where the electrocatalytic activity is mainly ascribed to PB compoment. From differential pulse voltammograms, a linear dependence of the current on the ascorbic acid concentration up to 4 mM has been obtained. These results clearly suggest that electrochemical step-by-step preparation procedure of hybrid inorganic-organic coating is a versatile tool for electrochemical sensors preparation.

# Electrochemical behaviour of biochemically active compounds on Bi(*hkl*) | base electrolyte interface

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Electrochemical behaviour of D-ribose, uracil and adenosine-5'-triphosphate ($ATP^{2-}$) anions on electrochemically polished Bi(*hkl)* single crystal electrodes has been studied by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and *in situ* STM methods [1-5]. The adsorption kinetics depends on the electrode potential and concentration of compound in solution and mainly the mixed kinetics (comparable rates of adsorption and mass transfer steps) has been observed in the region of adsorption-desorption peaks. In the region of maximal adsorption the mass transfer limited process (diffusion) prevails for dilute organic compound solutions. However, in more concentrated solutions the 2D-layer or 3D phase transition processes take place characterised with the anomalous steps at moderate ac frequencies in Nyquist plots, explained by the so-called anomalous diffusion processes inside the compact layer of organic adlayers [1-6]. The values of the limiting Gibbs adsorption, Gibbs adsorption energy, interaction constant in the Frumkin isotherm, zero charge potential shift due to the organic compound adsorption, effective dipole moment, coefficient of partial charge transfer and other adsorption parameters have been obtained and compared with the corresponding values for Hg | aqueous electrolyte interface [7]. Comparison of adsorption data for compounds investigated shows the noticeable dependence of the adsorption parameters on the molecular structure and chemical nature of functional group of adsorbate studied. Dependence of the zero charge potential shift $\Delta E_{\sigma=0}$, due to the organic compound adsorption, on the surface coverage $\theta$ has been discussed with the aid of Nikitas et al. [8] model. It was found that the shape of $\Delta E_{\sigma=0},\theta$ — plots depends on the hydrocarbon chain structure, as well as on the chemical nature of functional group of organic compound studied. Influence pH of the base electrolyte solution and crystallographic structure of the electrode surface on the adsorption parameters has been demonstrated and discussed.

**References**

1. E. Lust, A. Jänes, K. Lust, J. Electroanal. Chem. 449 (1998) 153.
2. A. Jänes, E. Lust, Electrochim. Acta 47 (2001) 967.
3. A. Jänes, K. Lust, E. Lust, J. Electroanal. Chem. 548 (2003) 27.
4. H. Kasuk, G. Nurk, K. Lust, E. Lust, J. Electroanal. Chem. 550-551 (2003) 13.
5. H. Kasuk, G. Nurk, K. Lust, E. Lust, J. Electroanal. Chem. 580 (2005) 128.
6. J. Bisquert, A. Compte, J. Electroanal. Chem. 499 (2001) 112.
7. V. Brabec, S.D. Christian, G. Dryhurst, J. Electrochem. Soc.125 (1978) 1236.
8. P. Nikitas, A. Pappa-Louisi, J. Electroanal. Chem. 385 (1995) 257.

# NEW NANOSTRUCTURED CU-CONTAINING POLYMER SYSTEM AS CATALYSTS FOR $O_2$ ELECTROREDUCTION

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The most efficient catalysts are the molecules which exist in non-equilibrium state. The presence of the polymer backbone stabilizes non-equilibrium state because the polymer itself is the system with slow attainable equilibrium state.

Cu-containing polymers with biquinolyl (biQ) fragments in the main chain were synthesized using sacrificial anodes. Formation of the Cu(I) ions in the solution organizes the polymer backbone on the nanoscale level , due to chelating interactions of biQ fragments with Cu-ions.

The investigation of electrochemical and spectral properties of the Cu-polymer obtained, as well as quantum-chemical DFT calculations, revealed the formation of two types of coordination complexes, as dependent on the conditions of electrosynthesis: Cu(I) in the tetrahedral environment of two biquinolyls ($[Cu^I(PA)_2][BF_4]^-$) and Cu(I) with one biquinolyl ligand and two molecules of the solvent ($[Cu^IPAL_2][BF_4]^-$). The latter complexes are less stable but they are especially active as catalysts for the electroreduction of $O_2$ to $H_2O$. The surface interactions with graphite electrode stabilize catalytically active form of Cu-containing polymer complex thus making it very convenient for the application in catalytic process of $O_2$ reduction. The catalyst is stable in water and in organic solvents.

The mechanism of electrocatalytic process was elucidated from the electrochemical, spectral and DFT data.

# Electrochemistry and Electrocatalysis of Horseradish Peroxidase (HRP) and Hemin in Organic Media

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Previously, we have observed that the haem of HRP displays direct electrochemistry on pyrolytic graphite (PG) and glassy carbon (GC) electrodes ($Fe^{3+}/Fe^{2+}$ redox couple). Reproducible and stable electrochemistry of HRP was obtained in phosphate buffer as well as in a number of water miscible organic solvents which contained 5% (v/v) of aqueous buffer. An extensive study of the redox thermodynamics of HRP reduction ($E°'$, $\Delta H°'_{rc}$ and $\Delta S°'_{rc}$) was conducted using the modified electrodes.

In HRP, the haem redox centre is buried deep within the protein matrix of the molecule. The fact that the direct electrochemistry of HRP is observed leads to the suspicion that the haem group of HRP might be extracted from the protein. Indeed over the last number of years, a discussion has emerged in the scientific literature on the topic of possible haem extraction from other haem-proteins such as haemoglobin [1-4] when immobilised on carbonaceous electrodes. To investigate this possibility, control experiments were carried out using hemin chloride for electrode modification instead of HRP, and the hemin electrodes were tested in the same way as HRP electrodes.

The experimental values of $E°'$, $\Delta H°'_{rc}$ and $\Delta S°'_{rc}$ were very similar for both HRP- and hemin-modified electrodes and suggest that the haem is fully or partially extracted from HRP upon immobilisation on PG electrodes.

HRP- and hemin-modified PG and GC electrodes were used for the detection of hydrogen peroxide in aqueous and organic solvents. The electrodes modified with hemin exhibited a higher response (higher sensitivity) to hydrogen peroxide than the HRP-modified electrodes. Previously, it had been reported that haem (hemin) itself can act as an enzyme catalyst similar to peroxidases and similar intermediates are probably involved in the catalytic cycle [5].

A hemin sensor for the detection of peroxides in organic solvents was studied using rotating disc GC electrodes. The sensor was tested in a variety of water-miscible organic solvents, where the influence of the water content was also examined. The sensor was characterised by kinetic and analytical means. The hemin sensor provides advantages such as lower material cost, diminished biological degradation and simplicity of preparation when compared to an enzyme (HRP) based sensor.

REFERENCES:
1. de Groot, M.T.; Merkx, M.; Koper, M.T.M. *J. Am. Chem. Soc.* **2005**, *127*, 16224.
2. de Groot, M.T.; Merkx, M.; Koper, M.T.M. *Electrochem.Commun.* **2006**, *8*, 999.
3. Guto, P.M.; Rusling, J.F. *Electrochem. Commun.* **2006**, *8*, 455.
4. Brusova, Z., Gorton, Lo., Magner, E., *Langmuir*, **2006**, *22*, 11453.
5. Lötzbeyer, T.; Schuhmann, W.; Schmidt, H.-L. *Bioelectrochem. Bioenerg.* **1997**, *42*, 1.

# CV-SECM at a confined disk ultramicroelectrode

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This work concerns the study of ultramicroelectrode (UME) confinement in integrated chemical microsystems. The numerical simulation obtained in the case of cyclic voltammetry (CV) applied to a finite disk ultramicroelectrode confined in front of an insulating surface is discussed. This configuration corresponds to scanning electrochemical microscopy (SECM) in negative feedback configuration. We describe a new electrochemical method, with acronym CV-SECM, based on the coupling of cyclic voltammetry with scanning electrochemical microscopy. The results of the simulation show that adjusting the scan speed of the potential sweep allows the exploration of a controlled range of distance between the UME and the insulating surface. The reverse peak current obtained in cyclic voltammetry exhibits unexpected variations with the approach distance of the UME: (i) a regime of depletion of the electroactive reactant during the forward scan at short distance, associated to a decrease of the peak current (ii) a regime of accumulation of the electroactive product at larger distance, associated to an increase of the reverse peak current in comparison with the free diffusion regime.

The demonstrated ability of the CV-SECM method achieved in this work puts this method in the expanding domain of the time resolved scanning probe microscopy (TR-SPM), with a major advantage versus other SPMs: probing the chemical reactivity of the surface specimen under study. As an electrochemical reversal technique (like double potential step chronoamperometry), cyclic voltammetry could be effective in order to study short-live generated species in a confined geometry through the CV-SECM technique.

By the use of cyclic voltammetry in confined systems, the extraction of electron transfer kinetics and diffusion coefficients could be obtained from comparison of numerical simulation with experimental data.

The CV-SECM combination of voltammetry and of a high resolution micropositioning system allows handling simultaneously a high spatial resolution and a high temporal resolution.

# Simple Size-Sorting of Magnetic Nanoparticles

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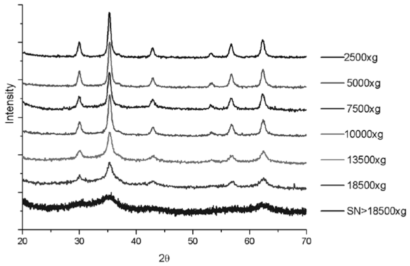
The magnetic ferrite nanoparticles are recently in focus of modern science and biotechnology due to their unique properties, giving them a variety of possible applications, including targeted drug delivery. Colloidal ferrites are usually synthesized in a relatively simple aqueous precipitation reaction, which can be easily adapted for big-scale preparations. However, the main disadvantage of this route is the high polydispersity of the product, unsatisfactory for further practical applications. Here, we propose an efficient way of sorting the particles by size. The colloidal suspension of nanoparticles is centrifuged at increasing rotational speed and the fraction sedimented on the bottom of the tube is collected after each run. The particles' size distribution and the efficiency of the process is estimated by agarose gel electrophoresis. Quantitatively, the mean size in each fraction is measured by Small Angle X-Ray Scattering and Powder X-Ray Diffraction.



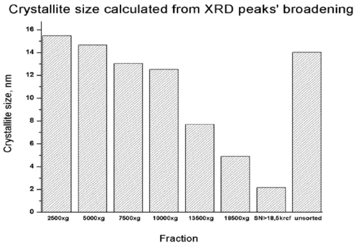
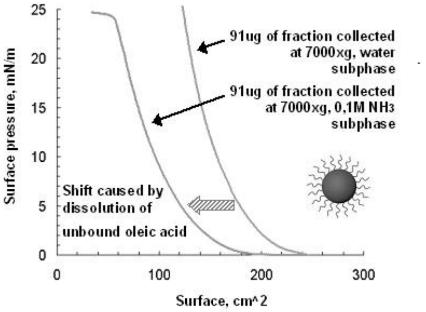


Fig 1 Powder XRD patterns of samples collected at increasing centrifugal forces. Widening of the peaks is observed. (1g=9.81m/s^2) Fig.2 Mean particle size calculated from peaks' broadening.



Sorted particles are further subjected to chemical modifications of their surface including, in first step, the adsorption of simple surfactant molecules and/or growth of the colloidal silica layer. Two-dimensional arrays, (on aqueous subphase, Langmuir-type) of particles grafted with oleic acid are transferred onto the solid substrate by Langmuir-Blodgett technique and characterized by neutron and X-ray reflectivity as well as IR spectroscopy. The second step includes the covalent attachment of drug molecules (e.g., anthraquinone derivatives) to the particle surface coated with silica. Magnetic properties allow for targeted medicine delivery while silica coating prevents the heavy-metal containing core from direct contact with the organism thus providing higher biocompatibility of these carriers.

# Rotating Disk Electrode as a Tool for Porosity and Catalytic Activity Determinations of Electroactive Polymer Films

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The main purpose of the present work was to develop some theoretical basis for using rotating disk electrode covered with an electroactive polymer film and bathed with a solution containing redox-particles (further, test ones) in order to judge about the film porosity or catalytic activity of the film respect to a chosen redox-reaction. Three different cases of test particles' participation in electrode reactions of a modified electrode were considered, namely (*i*) reduction/oxidation on a disk substrate as a result of particles' permeation through the film pores, (*ii*) heterogeneous reaction on the film/solution border, and (*iii*) volume reaction with the film fragments including of nano-structural ones. The recent modelling of charge transfer processes within electroactive films was a starting point of the relevant analysis [1,2]. As to its results, they are reduced in short to the following. The observed limiting currents on a rotating disk electrode should be strongly proportional to the concentration of test particles if the film is porous and the electrode reaction proceeds at the substrate. In case of reactions proceeding on either the film/solution border or within the film interior there must be the more deviations from such proportionality the more the concentration of test particles. Based on these and some additional consequences, we have determined the porosity and catalytic activity of a series of polymer films.

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[1] V.V. Malev, O.V. Levin, M.A. Vorotyntsev, Electrochim. Acta 52 (2006) 133
[2] V.V. Malev, O.V. Levin, M.A. Vorotyntsev, Elektrokhimiya (2007) (*Russian*, in press)

# Towards Nano-patterned DSA®

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Dimensionally Stable Anodes (DSA®) are used in large scale for production of e.g. chlorine and chlorate, very energy consuming processes. A typical anode consists of a Ti substrate coated with $Ti_{0.7}Ru_{0.3}O_2$. The success of DSA® is built on the large electrocatalytic area due to the cracked mud structure (figure 1a) [1]. A way to achieve a more efficient electrode is to control the surface topology. For industrial scale quantities of DSA®, this could be done by nanoimprint. The existing nanoscaled structure on top of the plaqettes has been observed [2] but the number of studies is limited.

We will present our plans towards nano-patterned DSA®, with emphasis of our first step which is the topographic characterisation of the anode surface on the nanoscale (figure 1b). We will present the connection between the surface topography and the manufacturing conditions.

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krävs för att kunna se bilden.

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**Figure 1 a)** Optical microscope picture of the cracked mud structure of the DSA® coating oxide, the bar at the top is 10 μm. **b)** Atomic force microscope picture of top of a plaquette, the picture is 300 nm wide and the greyscale is 6 nm.

[1] Trasatti, S., Electrochim. Acta 45 (2000) 2377

[2] Vallet, C.E., Appl. Phys. A. 65 (1997) 387

# Surface Immobilised Cyclodextrins: Molecular Recognition at Interfaces

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Self-assembled monolayers (SAMS) are convenient ways of ordering millions of molecules at an interface and SAMs incorporating host-guest functionalities are attractive platforms for supramolecular assemblies. Cyclodextrins (CDs) are bucket shaped molecules with hydrophobic interiors and hydrophilic exteriors capable of encapsulating suitable guests. At CD monolayers inclusion of electrochemically active guests can be easily studied provided solution phase signals are suppressed. However, the influence of surface immobilisation of the CD along with redox switching of the guest on the inclusion constant must be investigated to determine potential sensing or molecular electronic applications.

In this contribution, we present new SAMs comprising of di-6A, 6X- deoxy-6-(4-pyridylmethyl)amino- γ-cyclodextrin (γ-CD-(py)2) bound to a platinum surface via the pyridine linker where the defects between cavities are filled using an alkanethiol to minimise solution phase interference. A full characterisation of the layer formation and blocking properties has been carried out using both electrochemical and spectroscopic techniques. Raman and capacitance studies suggest the presence of both alkanethiol and pyridine bound molecules in the composite layer. Inclusion of the Cobalt complex shown in Figure 1 was demonstrated using cyclic voltammetry and followed a Langmuir adsorption isotherm from which inclusion constants at the interface were found. These constants were an order of magnitude higher for both redox states of the cobalt than those in solution, indicating that increasing the charge on the metal has little effect on inclusion.

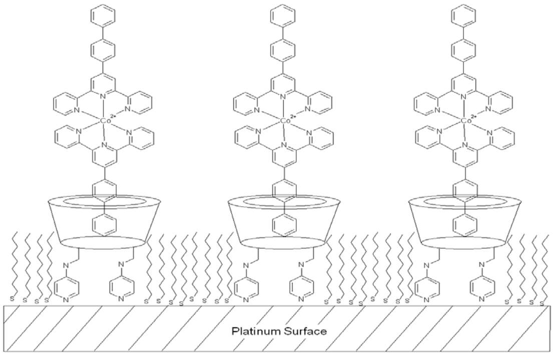

**Figure 1**: Inclusion of Co[biptpy]$_2^{2+}$ into CDs immobilised on a platinum surface where defects are sealed using 1-nonanethiol.

# An Evaluation of the Performance of a Microbial Fuel Cell Using Different Electrochemical Techniques

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The performance of a Microbial Fuel Cell (MFC) and the properties of the anode and the cathode have been evaluated using different electrochemical techniques. The MFC consisted of a graphite felt anode and a graphite felt cathode that was electroplated with platinum. The electrolyte was a buffer solution and the fuel was lactate. *Shewanella oneidensis* MR-1 was added to the anode compartment. Nitrogen was passed through the anode compartment, while air was passed through the cathode compartment. Ag/AgCl reference electrodes were placed in both MFC compartments to allow recording of EIS data for the anode and the cathode at the open-circuit potential (OCP) and at an applied potential.

Cell voltage (V) - current (I) curves were recorded using a potentiodynamic potential sweep between the open-circuit cell voltage and the short-circuit cell voltage at a scan rate of 0.167 mV/sec. Power (P) – V curves were constructed from the recorded I – V data and the cell voltage, Vmax, was determined, at which the maximum power could be obtained. Impedance spectra were collected for both the anode and the cathode before and after recording I – V curves. P – time (t) curves were obtained by applying Vmax or using a resistor between the anode and the cathode that would result in a similar cell voltage. Cyclic voltammograms (CV) were recorded at a scan rate of 25 mV/sec. Finally, anodic polarization curves were obtained for the anode and a cathodic polarization curve was recorded for the cathode. Separate tests were performed with 1) only the buffer solution, 2) the buffer solution and lactate, and 3) the buffer solution with lactate and MR-1.

The results of these tests showed that the power output of the MFC was greatly increased in the presence of MR-1. It was monitored for about three weeks with periodic additions of lactate and it was found that constant power density was maintained over several 12 h periods during this time. Additionally, the impedance data for the anode and the cathode did not indicate any significant changes of the electrode properties as a result of these tests. Lastly, the anodic polarization curves showed that the large negative shift of the OCP observed for the anode in the presence of MR-1 was accompanied by a large increase in the anodic reaction rate.

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# Probing the Electronic Properties of Soluble Carbon Nanotubes by Electrochemistry

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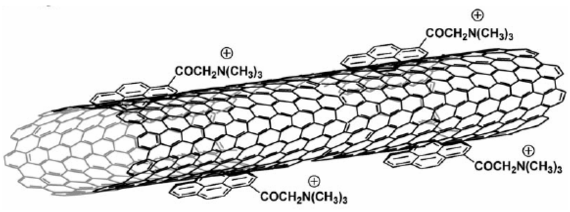
The investigation of the structural, physical and chemical properties of carbon nanotubes (CNTs) have drawn considerable attention, not only for their unique features, but also because of their promise in the area of new nanostructured materials with outstanding potential applications.

So far, the redox properties of CNTs have been mostly explored using the nanotubes themselves as electrode material. Such an approach, although it provides useful information on the performance of CNTs as active components of devices for energy storage and production, biosensing etc, does not give many insights on the electronic properties of single CNTs and their inter-tubes interactions occurring within the bundles.

The electrochemical approach used in this work allows the investigation of the electronic features of isolated (unbundled) CNTs in solution, which can usefully complement those provided by spectroscopy. The electronic properties of a wide class of soluble single and multi wall CNTs, which are either pristini [1] or covalently and non-covalently functionalised, have been extensively probed by different electrochemical and (combined) spectro-electrochemical techniques [2,3].



[1] A. Penicaud, P. Poulin, A. Derre, E. Anglaret, P. Petit, *J. Am. Chem. Soc.*, *127*, **2005**, 8.
[2] D.M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci, N. Tagmatarchis, D. Tasis, E. Vàzquez, M. Prato, *Angew. Chem. Int. Ed.*, *42*, **2003**, 4206.
[3] D.M. Guldi, E. Menna, M. Maggini, M. Marcaccio, D. Paolucci, F. Paolucci, S. Campidelli, M. Prato, G.M.A. Rahman, S. Schergna, *Chem. Eur. J.*, *12*, **2006**, 3975.

# Label free genonanosensor based on carbon nanotubes.

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In the last decade, the synthesis of various nanomaterials such as nanowires, nanotubes and nanocrystals has attracted immmense attention due to their potential to serve as building blocks for emerging nanoscale biosensor devices. In this work we design and test carbon nanostructured materials for the development of a geno-nanosensor. The carbon nanotubes are promising materials for highly sensitive DNA detection, because they have unique electric properties that are suitable for use as electrochemical biosensors. The electrochemical characteristics of the nanomaterials were obtained studying the electron transfer rates of potassium ferricyanide redox couple under different experimental conditions in Cyclic Voltammetry (CV) experiments. Moreover, Scanning electrochemical Microscopy (SECM) has been employed in the feedback mode to increase the information regarding the electrochemical behaviour of the carbon nanostructured materials. For this purpose, different electrochemical redox mediators were tested. As reported in literature, SECM has proven powerful for the measurement of the conductivity of ultrathin films and local electron transfer kinetic. Functionalized CNT-COOH was used for covalent DNA-probe immobilisation. The immobilised oligonucleotides are complementary to the sequence of the most common inserts in the GMOs: the Promoter 35S. The biosensor format involves the immobilisation of an inosine-substituted (guanine-free) probe onto the carbon nanotubes sensor surface, the hybridisation reaction and the direct square wave voltammetric detection of the duplex formation through the measurement of the oxidation peak of the guanine of the target sequence. Careful attention to the probe immobilisation conditions is crucial for minimising the guanine signal due to the non-specifically adsorbed sequences. Other relevant experimental parameters such as ionic strength, hybridisation time, the use of hybridisation accelerators were examined and optimised.

# Synchrotron X-ray Studies of Surface and Bulk Structure of Cathode Materials for Lithium-Ion Batteries

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With intercalating $LiCoO_2$ cathodes and carbon anodes it was possible to develop lithium-ion batteries. During charge to 4.2 V, approximately 50% of the $Li^+$ ions are removed from the $LiCoO_2$ and are transferred to the carbon anode. The process is reversed during discharge. $LiCoO_2$ cathodes are excellent for applications such as cell phones and laptop computers. However, Co is expensive and its price is volatile. A major search is underway to find other cathodes. Promising cathodes are $LiNi_{0.5}Mn_{0.5}O_2$, $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$ and $LiFePO_4$. Like $LiCoO_2$, $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ are layered materials with a trigonal symmetry (space group R3m), $LiMn_2O_4$ has a cubic spinel structure (Fd3m), and $LiFePO_4$ has an olivine orthorhombic structure (Pnma). $LiFePO_4$ has excellent thermal stability, even in the fully charged state.

In our present studies we have used both *in situ* and *ex situ* X-ray absorption spectroscopy (XAS) to study charge compensation in the cathode material when $Li^+$ ions are removed from the cathode during charge. This has included *in situ* XAS with hard X-rays (6000-9000 eV) at the K-edges of Mn, Fe, Co and Ni and *ex situ* soft X-ray (400- 1000 eV) XAS at the O K-edge and the Mn, Fe, Co and Ni $L_2$- and $L_3$- edges. In XAS the electron core hole can relax through two channels, one is the emission of an Auger electron, the other a fluorescent X-ray. The escape depth for the Auger electrons is ~50 Å, whereas the escape depth for the fluorescent X-rays is ~3000 Å. By doing XAS measurements simultaneously in the partial electron yield (PEY) mode and the fluorescence yield (FY) mode it is possible to get information on both the surface and bulk of the material. In the case of $Li_{1-x}Co_{1/3}Ni_{1/3}Mn_{1/3}O_2$, XAS at the Mn, Fe and Ni K-, $L_2$- and $L_3$- edges indicated that there is little or no charge compensation on either Mn or Co. Throughout charge, the Mn and Co remained as $Mn^{4+}$ and $Co^{3+}$, while Ni was oxidized from $Ni^{2+}$ to $Ni^{4+}$. XAS results at the O K-edge indicated further charge compensation by holes on oxygen that is associated with Co. Comparison of PEY and FY soft X-ray XAS at the O K-edge on $LiNiO_2$ showed major differences between the surface and the bulk. The surface contained $Ni^{2+}$ whereas the bulk contained only $Ni^{3+}$. These differences increased, over time, when the material was stored in the laboratory. Heat treatment of the material at 700°C, under oxygen for 5h, eliminated the differences.

Time resolved X-ray diffraction (XRD) was done on charged cathodes both in the presence of electrolyte and after washing and drying. The results showed that $Li_{0.05}FeO_4$ is much more thermally stable than $Li_{0.33}Ni_{0.5}Mn_{0.5}O_2$.

The work at BNL was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U. S. Department of Energy under Contract Number DE-AC02-98CH10886. This work was done at Beam Lines X7A, U7A, X11A, X18A, X18B and X19A at NSLS.

# Development of Stable Dehydrogenase-based Bioanodes

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This research has focused on developing an ethanol/oxygen biofuel cell with increased lifetimes using a dehydrogenase-based bioanode. This type of biofuel cell can be tailored to harness energy from any biofuel (including glucosa, sucrose, fructosa, soybean oil, glycerol, etc.) by altering the choice of dehydrogenase enzyme. In a biofuel cell, both the anode and the cathode can employ biological catalysts (enzymes) instead of traditional fuel cell catalysts (heavy metals). My research group has focussed on the development of bioanodes with stabilized enzymes for increasing active lifetimes. My research group has developed an ethanol/oxygen biofuel cell that employs immobilized alcohol dehydrogenase (ADH) and aldehyde dehydrogenase (AldDH) enzymes using $NAD^+$ as a coenzyme at the anode while the cathode catalyst was platinum. The enzymes are immobilized in a quaternary ammonium bromide treated Nafion membranes that provides a micellar pore structure for immobilizing the enzyme, but also provides a buffered pH for the modifying layer. The ion exchange capacity and transport properties of the quaternary ammonium bromide treated Nafion membranes have been previously studied. This research has focused on the studying the effect of enzyme immobilization on the transport properties of the membrane. The research has also focused on optimizing the bioanode to increase current densities and characterizing the active lifetime of the enzymes and coenzymes within the quaternary ammonium bromide treated Nafion membrane. Finally, the research has focussed on the investigation of different mediator systems and different methods for mediator immobilization for this system. Electropolymerized dyes (methylene green, methylene blue, azure C, etc.) have been investigated as mediators, along with binding of the mediator dye to polymeric backbones.

# Electrochemically Deposited Hydroxyapatite Coatings Implanted with $N^{4+}$ Ions

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Ceramic based on hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is very interesting according to possibility of use as biomedical material [1]. Deposition of HA coatings on titanium or titanium alloys has been achieved by a number of methods including plasma spraying, pulse laser deposition, sol-gel coatings, electrophoretic deposition, biomimmetic coatings. Electrophoretic deposition (EPD) has becoming very interesting because this method allowed the formation of thin films with controlled thickness. The mechanical properties of electrodeposited HA coating on titanium (e.g. hardness, elastic modulus) are poor. Ion-beam implantation was employed with the aim to improve the mechanical characteristic of HA coating on titanium.

Hydroxyapatite powder was synthesized by dissolving appropriate amount of $CaCl_2$, $Na_2H_2EDTA\ 2H_2O$, $NaH_2PO_4$ and urea. The solution was annealed at 160 °C during 3 h in sealed tube. The particles were further washed with distilled water and dried at 105 °C during 2 h [2]. For the preparation of HA suspension, 1.0 g HA powder was added into 100 ml ethanol. With the aim to increase the stability of the suspension, 10% HCl was added until pH value 2.0 was reached. The suspension was treated by an ultrasonically treatment for 30 min. Hydroxyapatite coatings were electrodeposited on titanium from HA suspension at constant voltage of 30 V and for deposition time of 30 s. After deposition, the HA coatings were implanted with $N^{4+}$ ions at three different constant dose of $10^{15}$, $10^{16}$ and $10^{17}$ $cm^{-2}$ with energy of 60 keV. Implanted HA coatings on titanium were characterized by X-ray diffraction (XRD) analysis. According to XRD results, the influence of ion implantation can be observed as a shifting of characteristics peaks at 2θ 26° and 34°, as well as the changes of their intensities. From the XRD results the relative intensities were calculated. The values of relative intensities for peaks at 2θ 26° and 34° decrease with increasing doze of implanted ions. The both effects indicate the changes of HA coating cristalinity.

References:
[1] Y. Han, T. Fu, J. Lu, K. Xu, J. Biomed. Mater. Res. 54 (2001) 96.
[2] D. Stojanovi , B. Joki , . Veljovi , R. Petrovi , P. S. Uskokovi , . Jana kovi , J. Eur. Ceram. Soc. 27 (2007) 1595.

# Conducting polymer-supported platinum nanoparticles produced using a friendly chemical synthesis

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Metals nanoparticles play an important role due to their potential applications in electronic and optical devices[1], biosensors[2], catalyst[3], etc. Because of the environmental protection and the decreasing in natural resources, the development of fuel cells has monopolized the most of the studies about metal nanoparticles.

Because of the expensive price of the precious metals used as catalyst and the need of high active surface catalyst, the most of applications requires the use of finely divided metals particles. In this way there are a lot of synthesis procedures for obtaining metal nanoparticles; in most of them capping agents are required in order to prevent aggregation of nanoparticles, thus avoiding losses in active area and catalytic activity. Also, the immobilisation of growing particles on solid supports[4] emerge as an alternative procedure to solve the lost of catalytic activity.

Carbon posses unique conducting and structural properties, since it exists in several solid forms and allotropes; this makes it an ideal material for its use in fuel cells. Conducting polymers are also very interesting materials to being used as catalyser supports since they can be covalently modified with functional groups, which can influence the kind of interaction between the metal and the substrate. In most cases electrochemical methods have been used in order to incorporate metal particles on electrochemically produced conducting polymers. However, in several cases it has been shown that the electrogenerated polymeric layer does not cover the whole electrode surface, which can contribute to the electrocatalytic behaviour observed.

In the present work a method to obtain metallic nanoparticles over different supporting materials (carbon black and polyaniline) was studied. The resulting electrocatalysts were characterized by means of several techniques such as Transmission Electronic Microscopy, X-Ray diffraction, XPS and Cyclic voltammetry. The solid support employed didn't affect both the size particles and their dispersion. Finally, the performance of the catalysts in methanol oxidation was studied.

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References

[1] Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Meltzer, S.; Requicha, A. A. G.; Atwater, H. A.; Adv Mater 2001, 13, 1501.

[2] Park, S. J.; Lazarides, A. A.; Mirkin, C. A.; Braziz, P. W.; Kannewurf, C. R.; Letsinger R. L; Angew Chem Int Ed 2000, 39, 3845.

[3] Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; ElSayed, M. A.; Science 1996, 28, 1924

[4] Chen, M.; Xing, Y.; Langmuir 2005, 21, 9334

# Inkjet Printing: Novel Fabrication Approach for Sensors based on Conducting Polymer Nanoparticulate Ink

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Inkjet printing is attracting considerable interest as a manufacturing technology with applications in fields outside its traditional use in printed text and graphics. Its future potential applications are projected to range from fabrication of polymer electronic components, organic light-emitting diodes, electrochromic displays, sensors, and microarrays for biological screening. By moving from other conventional deposition techniques to inkjet printing, unique advantages such as simplicity, high speed, compatibility with a wide range of substrates, non-contact patterning, additive properties (low waste), ability to deposit very small droplets (2 - 12 pl), and low cost can be realised.

Inkjet printable nanodispersions of the conducting polymer, polyaniline (PANI) have been recently synthesised by ourselves[1]. Until breakthroughs such as this, commercial applications employing PANI materials have been seriously hindered, despite its vast potential in areas such as sensors, rechargeable batteries, light-emitting diodes, corrosion protection of metals and gas separation membranes. This is due to the bulk polymers inherent lack of processability. Using a nanomaterial-based approach to develop a printable ink will overcome this barrier. Coupling the use of our nanoparticle-based inks with the technique of inkjet printing enables a practical route for fabrication of low-cost, manufacturable electronic devices such as sensors.

This research demonstrates the versatility and ease of deposition of polyaniline nanoparticulate inks using inkjet printing. Thin continuous films of PANI have been deposited onto flexible electrode substrate for electrochemical sensor and biosensor development. These films have been characterised in terms of their physical and electrochemical properties to truly demonstrate the high quality and level of control that inkjet printing, in combination with a suitable nanomaterial-based ink, can impart. A sensor application on the nano-based, low-cost sensor platform for ammonia has been demonstrated.

[1] Ngamna, O., Morrin, A., Moulton, S., Killard, A.K., Wallace, G.G., Smyth, M.R. (2007). *Submitted to Advanced Functional Materials*

# Nano-Cauliflowers: A Nanostructured Polyaniline-modified Screen-printed Electrode with a Self-assembled Polystyrene Template and its Application in an Amperometric Enzyme Biosensor

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This research examines a nanostructuring approach for fabricating polyaniline (PANI) films for enhanced electrochemical biosensing. Unique properties of conducting polymers only become apparent at the nanodimension - higher conductivity and more rapid discrete electrochemical switching processes. The route to this particular nanoarchitecture involved an in-situ nanostructuring of bulk polymer. An electrochemical template synthesis was used to create a highly ordered nodular cauliflower-like structure.

Polystyrene (PS) nanoparticles were self-assembled onto a PANI-modified SPE with the help of the negatively charged polyelectrolyte poly(sodium 4-styrenesulfonate) (PSS) and positively charged poly(diallyldimethylammonium chloride) (PDDA). The self-assembled PS nanoparticles could then act as a template for the electropolymerization of an additional layer of PANI. It was found that the additional layer of PANI preferred to grow around the PS nanoparticles, and a highly nodular, 'cauliflower-like' nanostructure of PANI was thus formed on the electrode surface, which was characterized by scanning electron microscopy (Fig. 1). The SPE modified with the nanostructured PANI (nano-PANI) was further used for the immobilization of horseradish peroxidase (HRP) and developed into a biosensor for hydrogen peroxide. Under optimized conditions, the proposed biosensor exhibited a fast response time of about 5 s, a linear range from $2.5 \times 10^{-6}$ to $1.9 \times 10^{-4}$ μM with a detection limit of 0.36 μM, and a high sensitivity of 41.0 μA $\text{mM}^{-1}$ due to the benefits of the nanostructured PANI.

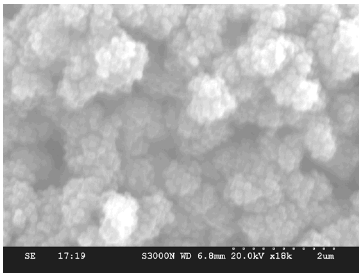

Fig. 1 Scanning electron microscopy of the prepared polyaniline nano-cauliflowers.

# Composite coatings with improved corrosion behavior obtained by electrolytic codeposition of copper with $Al_2O_3$ nanoparticles

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In plating industry, one of the ways used to obtain metallic coatings with improved corrosion properties consists in the incorporation of inert micro- and nanoparticles (ex. $TiO_2$, $SiO_2$, $Al_2O_3$) in the metallic matrix. The particles confer to the composite layers improved corrosion and wear resistance. They facilitate good adhesion of paintings on metal and increase its hardness as well as the lifetime of the coatings [1-3].

In this context, the present work aims to obtain and to characterize composite copper coatings incorporating $Al_2O_3$ nanoparticles, with improved corrosion resistance and tribological properties, by using the co-electrodeposition method. This method to obtain composite materials has some interesting advantages: (i) possibility of rigorous control of the deposited layer thickness; (ii) control of deposition speed; (iii) work at room temperature; (iv) use of accessible equipments. Moreover, the electrodeposition is suitable for obtaining non-uniform films on substrates with complex shapes (*e.g.* deposition only on some surfaces of the substrate, deposition on porous profiles etc.) [4].

In a first step, by using electrochemical investigation methods such as cyclic voltammetry, rotating disc electrode technique and electrochemical impedance spectroscopy, a fundamental study of the co-electrodeposition of copper with $Al_2O_3$ nanoparticles on steel was performed. The effects of the solution composition and concentration, the hydrodynamic conditions and the nanoparticles characteristics on the properties of the electrodeposited material were investigated.

In a second step, the corrosion behaviour of the $Al_2O_3$-copper composite coatings was examined by chronopotentiometry and hydrodynamic voltammetry (Tafel interpretation of polarization curves).

References

[1] J. Fransaer, J.P. Celis, Galvanotechnik, 92 (2001) 1544.
[2] A. Hovestad, L.J.J. Jansen, J. Appl. Electrochem., 25 (1995) 519.
[3] M. Musiani, Electrochim. Acta, 45 (2000) 3397.
[4] K. I. Popov, S. S. Djokic, B. N. Grgur, Fundamental Aspects of Electrometallurgy, Kluwer Academic/Plenum Publ. NY, (2002).

# Nanoarchitecture of self-assembled gold cubes

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The ability to manipulate the morphology of nanoparticles to fabricate functional nanoarchitectured electrode assemblies is a challenge for material scientists and electrochemists. In particular gold nanoarray electrodes have potential applications in chemical and biological sensing, microelectronic devices, catalysis and photonic crystals [1-3]. A simple method has been developed to synthesise a 3D array of gold nanocubes on a carbon substrate. It was found that the destabilization of a chloroformic dispersion of tetraoctylammonium bromide-stabilized gold nanoparticles by ethanol followed by appropriate heat treatment transforms the nanoparticles into nanocubes which spontaneously self-assemble. The stability of the nanocube assembly was investigated in reductive and acidic media. Characterisation by TEM will be presented.

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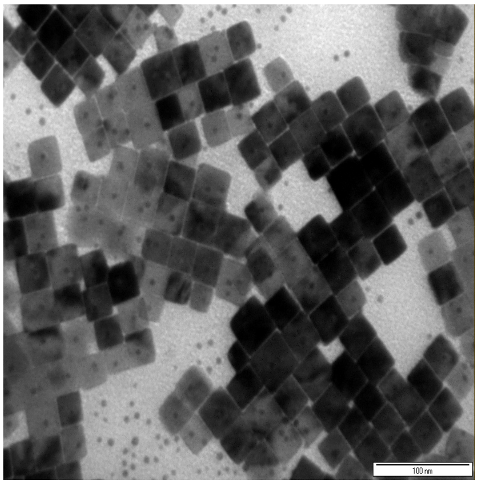
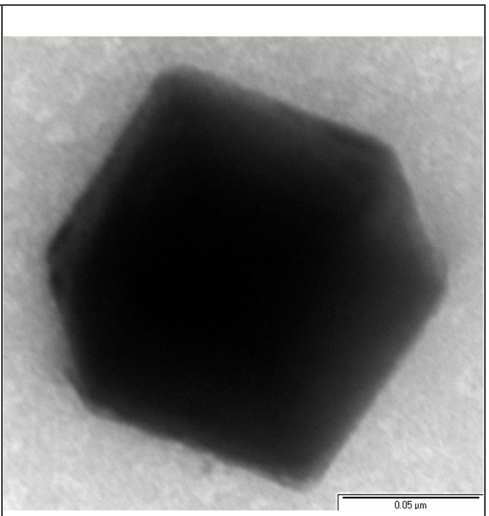
|  |  |
| Figure 1. TEM image of gold nanocube array on carbon-coated copper grid recorded at 80 kV. | Figure 2. TEM image of gold nanocube on carbon-coated copper grid tiltled by $40^o$ recorded at 80 kV. |

**References**

[1] C. Huang, Y. Wng, P. Chiu, M. Shih, T. Meen, Mater. Lett. 60 (2006) 1896.

[2] A. Escoria, A. Dhirani, J. Electroanal. Chem, in press.

[3] Y. Guo, H. Zhang, J. Hu, L. Wan, C. Bai, Thin Solid Films 484 (2005) 341.

# Modified Oxide Graphite as Special Electroactive Material

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Recently a novel electroactive material with special nanostructure was developed [1]. The material is oxide modified graphite (OMG). The first stage in the OMG preparation consists in pulverization of proper natural graphite. Then this powder is treated with acid oxidizing solution, e.g. with mixture of sulfuric and nitric acids. The resulting product is graphite oxide with common formula $C_x(OH)_y(H_2O)_2$. The second stage consists in modification of the graphite oxide with aqueous solution of perchloric or peroxydisulfuric acid. Finally, such a modified product is heated up to 250 °C. During this heat treatment considerable swelling up occurs with gigantic volume expansion. Specific volume of OMG amounts to 400 $cm^3$/g. The principal feature of OMG is its special structure. The OMG particles with typical size about 25−50 µm have so-called cabbage-head-like structure. They are formed from leaves with thickness of 50−100 nm and inter-leaves space is about 1 nm. Therefore this dimension is comparable with size of macromolecules. The probability of macromolecules enters into the inter-leaves space depends on electric charge. Specific surface area of OMG is close to 2000 $m^2$/g. In principle OMG could be used in various sensors and biochips.

Reference:
1. Russian Patent No. RU 2198137, 26.04.02.

# Laccase - syringaldazine modified carbon - silicate composite electrode for dioxygen reduction

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Laccase catalyses four electron reduction of dioxygen to water [1]. This property makes this enzyme one of the possible candidates as biocatalyst on cathode for membraneless biofuel cell [2]. Syringaldazine (3,5-dimethoxy-4-hydroxybenzaldehydazin) is the compound used for determination of laccase activity [3]. It is one of the possible mediators for this enzyme.

Voltammetrically stable syringaldazine modified ceramic carbon electrode (CCE) was obtained by sol-gel processing of hydrophobic methyltrimethoxysilane based sol with dissolved syringaldazine together with dispersed graphite particles [4]. Laccase from *Cerrena unicolor* was encapsulated within thin hydrophilic tetramethoxysilane-based silicate film on the CCEs surface [5].

The electrochemical behaviour of electrode without laccase was monitored using cyclic and differential pulse voltammetry. The redox potential of syringaldazine depends on *pH*. Laccase - syringaldazine modified electrode exhibits catalytic activity towards dioxygen. Obviously, water insoluble syringaldazine immobilized within hydrophobic matrix of CCE shuttles electrons between carbon particles and enzyme.

Maximal current densities of electrocatalytic dioxygen reduction are observed in lower *pH* range (ca. 4.8), however in physiological *pH* range electrode is also active and exhibits better stability than ABTS modified electrode [6].

[1] C.W. Lee, H.B. Gray, F.C. Anson, B.G. Malstrom, *J. Electroanal. Chem. 172* (1984) 289.
[2] A. Heller, *Phys. Chem. Chem. Phys. 6* (2004) 209.
[3] K.A. Holm, D.M. Nielsen, J. Eriksen, *J. Autom. Chem. 20* (1998) 199.
[4] L. Rabinovich, O. Lev, *Electroanalysis 13* (2001) 265.
[5] R.A. Simkus, V. Laurinavicius, L. Boguslavsky, T. Skotheim, S.W. Tanenbaum, J.P Nakas, D.J. Slomczynski, *Anal. Lett. 29* (1996) 1907.
[6] W. Nogala, E. Rozniecka, J. Rogalski, M. Opallo *Electrochem. Commun. 8* (2006) 1850.

# A Novel method for Microfabrication without photolithography

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Microfabrication is a processing technology for the production of devices in the micrometer range. It has found wide-spread application in many fields, including semiconductor and Microsystems production and in the manufacture of optoelectronic devices. The most common microfabrication technique is photolithography. This is a multi-stage process, which leads to micropattern on the substrate's surface. Photolithography incurs high capital and running costs, the former resulting from the fact that it needs to be carried out in a clean room, and the latter from its sequential nature which requires optimisation at every stage, and high consumption of substrates, photoresist and solvents, with a high environmental impact. We addressed these shortcomings by developing a new electrochemical process for micropattern transfer. In this technique, an anode is placed in an electrochemical reactor in close proximity to a tool, which is the micropatterned cathode. Although the anode is etched over its entire surface, it will etch at a higher rate on the areas opposing the micro-features on the cathode, thus replicating the pattern on the cathode. Feasibility studies were successfully carried out on copper substrates etched in a copper sulphate electrolyte with and without the addition of sulphuric acid [1]. We have extended the application of electrochemical micropattern transfer to titanium which is widely used in dental and orthopaedic implants. From a biomedical perspective, titanium is a unique metal, in that not only does it not cause a ‘foreign body’ response when implanted into bone, it can in fact act as a scaffold around which bone-healing occurs, resulting in the integration of the prosthesis into the patient's skeleton. This has major medical implications since implant rejection and loosening are the commonest causes of failure of operations like hip and knee replacement. However, titanium's ability to act as a scaffold for the bone-forming osteoblast cells and thus its capacity for osteo-integration is determined by the metal's micro-surface structure at the bone-implant interface. In this study we investigated the utility of the electrochemical process in etching titanium surfaces, and the compared different surfaces in respect of their ability to integrate with rat osteoblast cells *in vitro*. The titanium surface was manipulated in a 3-electrode flat cell in a 2M sulphuric acid in methanol electrolyte by varying the potential and processing times. Stylus profilometry, atomic force microscopy and environmental scanning electron microscopy were used to characterise surface morphology. Cell morphology and degrees of cellular proliferation and bone formation on titanium were measured with fluorescence microscopy and compared using analysis of variance. Samples treated at 3 and 5V (vs. SCE) encouraged the greatest degree of cellular proliferation and bone formation ($p<0.05$; ANOVA). Electrochemical micropattern transfer can be successful in etching specific patterns on the surface of titanium that enhance its biocompatibility and osteo-integration. This in turn has major implications for improving the design and longevity of orthopaedic and dental implants.

# Redox polymer mediation of enzymes for amplified amperometric detection of DNA hybridization.

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Sensors and assay for the detection of DNA hybridization are useful tools in clinical and environmental diagnostics. A major problem in detecting DNA in such samples is that the concentration of DNA is lower than the detection limit of most analytical techniques. Electrochemical methods, coupled to enzyme amplification, may prove a viable alternative to optical and radio-labelled DNA diagnostic techniques. We detail in this presentation our strategy to achieve highly sensitive amperometeric assays for the detection of nucleic acids, based upon recognition surfaces formed by co-immobilization of a redox polymer mediator and DNA probe sequences on gold electrodes. The recognition layer consists of an osmium-based redox polymer and a model single DNA strand cross-linked and tethered to a gold electrode via an anchoring self-assembled monolayer (SAM) of cysteamine. Hybridization between the immobilized probe DNA of the recognition surface and a biotin-conjugated target DNA sequence (designed from the ssrA gene of *Listeria Monocytogenes*), followed by addition of an enzyme (glucose oxidase)-avidin conjugate, results in electrical contact between the enzyme and the mediating redox polymer. In the presence of glucose, the current generated due to the catalytic oxidation of glucose to gluconolactone is measured, and a current response is obtained that is binding dependant. At gold macro-electrodes, the sensor response increases linearly with increasing concentration of target DNA in the range of $1 \times 10^{-9}$ M to $2 \times 10^{-6}$ M [1]. In an attempt to decrease the detection limit we describe the use of gold microelectrodes. The sensor response increases linearly with increasing the concentration of target DNA in the range $2 \times 10^{-15}$ to $2 \times 10^{-5}$ M. The obtained detection limit is circa 8.4 zmol ($10^{-21}$) in a 3.5 µL droplet and corresponds to a concentration of $2.4 \times 10^{-15}$ M of target DNA in the sample.

Regeneration of the recognition surface is possible by treatment with 0.25M NaOH solution. After re-hybridization of the regenerated surface with the target DNA sequence, >95% of the current is recovered, indicating that the redox polymer and probe DNA are strongly bound to the surface.

1. Kavanagh, P.; Leech, D. *Anal. Chem.* 2006, **78**, 2710.

# Carbon Paste Electrode Containing Organically Modified MCM-41; Application for Detection of Ferrocyanide

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MCM-41 molecular sieves are a new class of mesoporous aluminosilicates, having regular, well-defined and uniform channels with diameters between 1.5 to 10 nm. Their synthesis was first reported by researchers of the Mobil Oil Corporation [1]. These solids feature very high surface areas (up to about 1000 $m^2$ $g^{-1}$) with silanol groups in their internal surfaces. Organic functionalization of the internal surface of these materials by covalently grafting of various organic species into the channel walls has been widely employed to anchor specific organic groups onto surface silanols, typically using organochlorosilanes or organoalkoxysilanes as precursors for the surface modifications [2].

The organically modified mesoporous aluminosilicates have recently attracted considerable attention and gave rise to a wide range of applications, mainly in analytical separations, electrochemistry and sensors [3, 4]. Using organically modified porous adsorbents as electrode modifiers and proper choice of the organofunctional groups increase the sensitivity of the resulting modified electrodes for preconcentration analysis [5,6].

In this work we prepared aminopropyl-grafted MCM-41, and characterized with XRD and FTIR methods. Experimental results show that carbon paste electrode modified with this material has observational anion exchange capacity after protonation of amine group in acidic medium; therefore we used this electrode for open circuit accumulation and voltmmetric determination of ferrocyanide in aqueous solution and investigate factors affecting magnitude of analytical signal.

## References:

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992)710.
[2] K. Moller, T. Bein, Chem. Mater.10 (1998) 2950.
[3] M.R. Jamali, Y. Assadi, F. Shemirani, et al, Analytica Chim. Acta 579 (2006) 68.
[4] A. Walcarius, Electroanalysis 13 (2001) 701.
[5] W. Xantasse, Electrochem. Commun. 7 (2005)1170.
[6] A. Walcarius, M. Etienne, S. Sayen, B. Lebeau, Electroanalysis 15 (2003) 414.

# A Sensor for Nitrite; Using a Carbon Paste Electrode Modified with Copper (II) Hexacyanoferrate (III)

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Nitrite ion is widely involved in environmental chemistry and public health, so its important role was recognized long ago. One of the most useful method for its determination is electrocatalytic reduction of it using a chemically modified electrode. On the other hand, metal hexacyanoferrate films resemble both redox organic polymers and zeolitic material and have been applied in chemistry and material science [1]. These well-organized inorganic films are well suited for electrochemical studies due to their simple preparative procedure, excellent stability, highly characterized structures and the ease by which interfacial properties can be controlled. Among them, Copper hexacyanoferrate has received considerable interest in electroanalysis due to its remarkable electrocatalytic property. It is an ion conductor with redox active sites [2].

In this work, the preparation and electrochemical characterization of a carbon paste electrode modified with copper (II) hexacyanoferrate (CuHCF) as well as its behavior as electrocatalyst toward the reduction of nitrite were investigated. The electrochemical behavior of the modified electrode and the electroreduction of nitrite were explored using voltammetry methods such as cyclic voltammetry and differential-pulse voltammetry. A quasi reversible redox couple with a mid point potential of 56 mV corresponding to $Fe\ (CN)_6^{-4}/ Fe\ (CN)_6^{-3}$ reaction observed.

These electrochemical techniques showed that CuHCF film can catalyze the nitrite reduction in acidic solution (pH=0.0). Linear voltammetric responses for nitrite were obtained in the concentration range from $10^{-4}$ M to $10^{-2}$ M and from $4\times10^{-6}$ M to $1\times10^{-3}$ M by using cyclic voltammetry and differential- pulse voltammetry with detection limits of $8\times10^{-5}$ and $1\times10^{-6}$ respectively.

**References:**

[1] S- M. Chen, C-M. Chano, J. Electroanal. Chem. 543 (2003) 161.
[2] W.T. Suarez, L.H. Marcolina, Microchemical J. 82 (2006) 163.

# Electrochemical Preparation of Platinum Nano-Wires and Their Application to Electrocatalysts for PEM Fuel Cells

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One of a promising way to improve the Proton Exchange Membrane Fuel Cells (PEMFCs) performance is the optimization of the material and structure used for the cathode catalyst. For example, many researchers have reported an one-dimension catalyst using carbon nanotube [1-2]. However, the nanotubes were not oriented perpendicular to the proton exchange membrane at suitable intervals, which is expected to improve gas diffusion and electronic conductivity.

In this study, we report the successful formation of Pt nanowires perpendicular and regular array to the membrane by electrodeposition through optimized deposition. We have investigated the relationship between the power density and the length of the wires.

An aluminum layer was formed on silicon wafers by sputtering. Alumina nanoholes were produced by anodic oxidation of aluminum. In typical conditions, an alumina nanohole film can be formed from a 0.3 mol/L sulfuric acid solution under the electrolytic potential of 25 V at 3 $^{o}$C [3]. A pore widening treatment involving immersion in a 5 wt.% phosphoric acid solution was performed for 20 minutes to make alumina nanoholes having an average pore size of about 20 nm. The Pt nanowires were deposited with the electrolytic potential of –0.8 V vs. Ag/AgCl at room temperature from a 0.03 mol/L Hydrogen hexachloroplatinate hexahydrate solution. The substrate was immersed in a 5 wt.% phosphoric acid solution again, because we formed a gap between wire and alumina. Moreover, the gaps were immersed into polymer electrolyte. A polymer electrolyte membrane was sandwiched between two of these substrates, and these three layers were directly assembled by hot pressing. Alumina nanoholes were completely dissolved in acid solution, we got the Membrane Electrode Assembly (MEA) with Pt nanowire.

Wires of platinum were grown on a polymer electrolyte membrane by transcription of electrodeposited nanowires into an alumina nanoholes (Fig.1). The maximum aspect ratio of Pt nanowires was accomplished by optimizing the conditions. The performance of the Pt nanowires as a cathodic electrode of a fuel cell was investigated using $H_2$ and Air. A high performance is obtained by high aspect ratio Pt-nanowire electrode. A linear relationship was observed between the power density and the length of the wires. The details of the research including platinum-alloy nanowires will be reported at this conference.

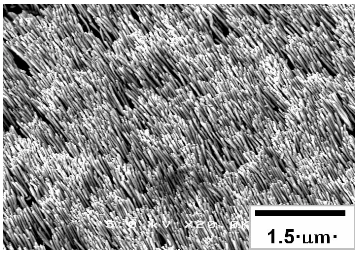

Fig.1 SEM surface-view images of Pt nanowires electrodeposited onto the membrane.

[1] G.L. Che, B.B. Lakshmi, E.R. Fisher, C.R. Martin, *Nature*, **393** (1998) 346.
[2] W. Li, X. Wang, Z. Chen, M. Waje, Y. Yan, *Langmuir*, **21** (2005), 9386.
[3] H. Masuda, K. Fukuda, *Science*, **268** (1995) 1466.

# Silicate confined ionic liquid modified electrode for anion preconcentration and biocatalysis

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Recently few attempts of covalent immobilisation of room temperature ionic liquids for catalytic purpose was reported in literature [1]. It employs immobilisation of ionic liquid having sol-gel precursor as cation [2,3].

Here analogous concept of designing highly dispersed ionic liquid modified electrode will be presented. The thin film preparation employs sol-gel processing of sol composed of ionic liquid with 1,3-alkylimidazolatotrimethoxysilane cation and tetramethoxysilane on ITO electrode surface. In order to increase electrode reaction efficiency for some experiments this step was preceded by deposition of the ITO nanoparticles (21 nm diameter) by subsequent immersion and withdrawal from their suspension [4].

It has been found that the prepared electrodes acts as anion exchanger for inorganic - $Fe(CN)_6^{4-}$ [5] and organic - 2,2'-azino-bis-(3-ethylbenzothiazoline) sulfonate ($ABTS^{2-}$ ) anions. Silicate confined ionic liquid electrode preconcentration ability and kinetics of his process depends on composition of the film and type of the anion. The amount of absorbed anion is substantially increased on the electrodes with predeposited ITO nanoparticles.

The electrode with immobilised $ABTS^{2-}$ was further modified with laccase from *Cerrena unicolor* encapsulated within silicate film [6]. These electrodes show catalytic activity towards dioxygen reduction [6,7].

1. M.H. Valkenberg, C. deCastro and W.F. Hölderich, Green Chem. 4 (2002) 88.
2. R. Ciriminna, P. Hesemann, J.l.J.E. Moreau, M. Carraro, S. Campestrini, M. Pagliaro, Chem. Eur. J. 12 (2006) 5220.
3. C.P. Mehnert, R. A.Cook, N.C. Dispenziere, M. Afeworki, J. Am. Chem. Soc. 124 (2002) 12932.
4. J. Niedziolka, K. Szot, F. Marken, M. Opallo, Electroanalysis in press.
5. P. Tien, L.-K. Chau, Y.-Y. Shieh, W.-C. Lin, G.-T. Wei, Chem. Mater. 13 (2001) 1124.
6. I. Zawisza, J. Rogalski, M. Opallo, J. Electroanal. Chem. 588 (2006) 244.
7. D. Quan, Y. Kim, W. Shin, J. Electroanal. Chem. 561 (2004) 181.

# Evidences of Opened Structures Formation During the Oxidation of Conducting Poly(o-Aminophenol).

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Poly(o-aminophenol) films were deposited on gold electrode in a 0.1 mol dm$^{-3}$ KCl solution at pH 1.2. The film is electrochemically active, reproducible and stable. The in situ FTIR analysis of the structural changes of the polymer during its redox process showed the existence of structures redox which involve the elimination and addition of protons coupled to an electronic transfer. Opened units are favored when the polymer is in its oxidized form and the closed units prevail in the polymer reduced. As the pH increases, the electrochemical activity from the polymer decreases; polymer becomes an insulator at about 5.0 pH units. This behavior can be observed in the FTIR spectra.

# Electrochemical relaxation loop, conformational energy and conformational memory. (Is brain memory stored by polymeric conformations?)

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Here we will present how the electrochemical oxidation/reduction of polythiophene (similar results are being obtained in our laboratory from different polythiophene and polypyrrole derivatives) by potential steps, in an electrolyte, from different cathodic potentials define relaxation loops. Unlike magnetic loops here both, the relaxation time (relaxation loop width) and the relaxation charge (relaxation loop height) can change, under control, in a continuous way as a function of the physical and chemical variables acting on the electrochemical reaction. According with the Electrochemical Stimulation of the Conformational Relaxations (ESCR) model (1), different conformational packed states of the folded polymeric chains in the film (different physical initial states) are attained by the cathodic reduction-packing. The subsequent electrochemical oxidation is under kinetic control of the conformational relaxation process. Through the electrochemical reaction we have developed a way to obtain both, the activation chemical energy for the polythiophene oxidation plus the conformational energy of the initial packed states of the folded chains.

The obtained conformational energy of the chains increases linearly for rising packed initial states of polythiophene films, attained by polarization at increasing cathodic overpotentials. Those results open the way to allocate (write) information (memory) to folded polymeric conformations, and to read this information by electrochemical reactions in soft, wet and reactive polymeric materials.

This elegant electrochemical methodology to obtain a so important magnitude as the conformational energy, moreover the possibility to control its variation in a continuous way by physical and chemical variables can be of interest for either, physicists, chemists, biologists, medical doctors, etc.

Our results open the possibility to apply similar theoretical treatments to the biological reactions most of then including conformational changes of biopolymers and, up to now, only qualitatively explained. Among those reactions emerge the possibility to store and read some kind of information on conformational structures in nervous channel proteins that give similar i/t responses as those showed by figure 2.

1.- TF Otero et Al. *J. Electroanal. Chem.* **394**, 211-216 (1995); *J. Phys. Chem.,* **101**, 3688-3697 (1997); Conducting polymers, electrochemistry and biomimicking processes. In *Modern Aspects of Electrochemistry*, **Vol. 33**, edited by Bockris, J. O'm. White, R.E. and Conway, B.E. New York , Pg. 307-434 (1999). *Handbook of Conducting Polymers (3rd Edition)*. Ed by Skotheim, T.A., Elsenbaumer. R.L. and Reynolds, J.R. Marcel Dekker Inc. 591-624 (2006).

# Blood Lead Analysis Using Nanostructured Screen-Printed Carbon Electrodes

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In this work, the surface of screen-printed carbon electrodes is modified with gold to get a nanostructured surface. The voltammetric behaviour of these nanostructured screen-printed carbon electrodes is studied.

The surface of the electrodes is modified in two different ways; by evaporation of a colloidal gold suspension on the electrode previously activated in basic media, or by gold electroplating applying a constant current.

The nanostructured screen-printed carbon electrodes constructed with the optimised experimental conditions are used for the electrochemical determination of lead in aqueous medium using anodic stripping square wave voltammetry. A shift of the potential of the anodic peak of lead towards more positive potentials is observed when screen-printed carbon electrodes are modified with gold. The analytical characteristics as limits of detection, linear ranges, reproducibility and the selectivity of the determination of lead in aqueous medium using these nanostructured screen-printed carbon electrodes are evaluated.

Finally, these nanostructured screen-printed carbon electrodes will be used for blood lead analysis using an internal standard.

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# Electronic sensor application of SWCNT network devices

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Single-wall canbon nanotubes(SWCNT) are very promising electronic material in the sensor field in addition to microelectronic and display field application. We have fabricated SWCNT network device based on the surface-programming method which enables us to make array device on the whole wafer. This technique can be realized on the flexible substrate, for example, transparent plastic substrate. The electrical property of SWCNT network device array was analyzed in terms of 2-terminal or 3-terminal field-effect transistor. At the moment, we tested our SWCNT network device in order to apply to a bio-chemical sensor. The simple gas like NO was introduced to verify its chemical sensing property and the typical biological sensing experiment was performed using anti-body and antigen coupling method.

# Monolayer synthesis of the ordered organic surface on a gold substrate

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Organic surfaces are typically less ordered and less thermally stable than their inorganic counterparts. However, the recent explosion of interest in this area has been fueled by advances in the creation of novel and flexible synthetic routes that enable the formation of very well-defined organic surfaces. Self-assembled monolayers are assemblies spontaneously formed by the immersion of an appropriate solid substrate into a solution of organic molecules.

In this study, the adsorption thermodynamics and kinetics of self-assembly of n-alkanethiol monolayers on a polycrystalline gold electrode were studied *in-situ* using electrochemical quartz crystal nanobalance and electrochemical impedance spectroscopy. The double layer capacitance was used to calculate the surface coverage as a function of time and the concentration of alkanethiol. The structural and electrochemical properties of alkanethiol monolayers were studied by contact angle measurements, Raman spectroscopy, and electrochemical measurements.

*Key words*: gold, n-alkanethiols, self-assembled monolayers, adsorption.

# Mesoporous Pt/Ru electrodes for direct methanol micro-fuel cells

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Direct methanol fuel cells are very promising devices for applications as power supply for portable electronic systems, medicine, communication and transport. They are characterized by a silent, continuous operation regimen, inexpensive fuel and low environmental impact. High performance electrochemically obtained anodes and cathodes are especially interesting because their *in-situ* construction capability, aiming to applications in micro watt fuel cells (μFCs) [1]. As recently demonstrated, adjacent electroplated anode-cathode [2], silicon based [3] and commercial membrane electrode assembly based [4], μFCs can operate successfully in a compact design for *on-board* applications. However, no special efforts have been made to optimize the catalyst characteristics in this type of design.

During the past years, new all-metallic mesoporous (MP) structures were synthesized by chemical [5] and electrochemical reduction [6] of metallic salts dissolved in the aqueous domains of a liquid crystal solution. Likewise, MP particles of Pt/Ru alloys [7] were obtained by chemical co-reduction (*ex-situ*).On the other hand, the Pt surface has been broadly modified by spontaneous deposition of Ru and results show that these electrodes improve twice the catalytic activity against conventional Pt/Ru alloys [8].

In this work, we propose a whole *in-situ* process for the production of greatly active Pt-Ru electrodes for practical *on-board* applications. These electrodes were obtained from electrochemical reduction of metallic salts dissolved in the aqueous domains of a liquid crystal solution by means of a potential step. Surface modification with Ru adatoms was carried out by spontaneous deposition from an aged solution of $Ru^{+3}$.

The electrochemical characterization of these Pt electrodes reveals a high efficiency for methanol electrooxidation, with a mass activity of 41 $Ag^{-1}$, which is improved up to 110 $Ag^{-1}$ when Ru adatoms are present as surface modifiers. These results support the viability of an *in-situ* building up for applications *on-board* fuel cell devices. The high current densities are related to low $CO_2$ conversion efficiencies, as it was established by using differential electrochemical mass spectrometry in a thin layer flow cell configuration (TLFC-DEMS).

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**References**

[1] S.J. Lee, C. Chien, S.W. Cha, R. O`Hayre, Y.I. Park, Y. Saito, F.B. Prinz. J. Power Sour. 112 (2002) 410.
[2] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka. Electrochem. Comm. 6 (2004) 562.
[3] G.Q. Lu, C.Y. Wang, T.J. Yen, X. Zhang. Electrochem. Acta 49 (2004) 821.
[4] R. Hahn, S. Wagner, A. Schmitz, H. Reichl. J. Power Sour. 131 (2004) 73.
[5] G.S. Attard, C.G. Goltner, J.M. Corker, S. Henke. R.H. Templer. Angew. Chem., Int. Ed. Engl. 36 (1997) 1315.
[6] J.M. Elliot, P.R. Birkin, P.N. Bartlett, and G.S. Attard. Langmuir 15, 22 (1999) 7411.
[7] A. Crown, C. Johnston, A. Wieckowski. Surface Science 506 (2002) L268.
[8] P. Waszczuk, J. Solla-Gullón, H.-S. Kim, Y.Y. Tong. V. Montiel, A. Aldaz, and A. Wieckowski. J. of Catalysis 203 (2001)1.

# Electrochemical Synthesis of Au Nanostructures in Modified Electrodes with Dendrimers and SAMs

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The synthesis of nanostructured materials using bottom-up approaches is a very challenging field of investigation. Its advantages over top-down nanofabrication are well recognized; the latter requires more elaborate physical methods and usually addresses fewer objects simultaneously. The bottom-up approaches rely significantly on the chemistry of systems, through molecular recognition and supramolecular interactions. The present work describes a method designed for the synthesis of Au nanostructures in modified Au electrodes. The modification procedure involves deposition of a self-assembled monolayer (SAM) of mercaptoundecanoic acid and/or an alkanethiol followed by the physical adsorption or covalent linkage of PAMAM dendrimers of generation 4. The dendrimer-SAM modified electrodes comprise the molecular template for Au electrodeposition through chronoamperometry. The topography of the modified electrodes was investigated by Atomic Force Microscopy (AFM) and Scanning Tunnelling Microscopy (STM) and its electrochemical behaviour was characterized by cyclic voltammetry. Preliminary results of current transients during Au electrodeposition, at distinct potentials provide interesting hints towards the smooth conditions envisioned for controlled Au deposition over the modified electrode template. Some reports of dendrimer – metal nanoparticle composite systems assembled at surfaces have appeared in the literature, but to the best of our knowledge, this attempt of producing metal nanoparticles "in situ" by electrochemical methods is novel. Further developments of this work involve the study of interactions between the synthesized Au nanostructures and organic cromophores using single-molecule spectroscopy.

# Silver Nanoparticles Obtained by Electrosynthesis in Aqueous Media under Protection of a Mix of Stabilizers

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Noble metals nanoparticles synthesis attracts an increasing interest due to their new and different characteristics as compared with those of macroscopic phase, that allow attractive applications in various domains, such as: optics, microelectronics, catalysis, information storage, energy conversion [1]. Moreover, nano-silver based colloidal solutions are particularly involved in environmental and biological applications due to their specific antimicrobial properties.

With this in view, the present paper presents some preliminary experimental results dealing with electrochemical synthesis and characterization of silver nanoparticles obtained in the presence of various stabilizers and co-stabilizers agents, such as: PVP [poly(N-vinylpyrrolidone)] [2,3] with molecular weight of 10000, 25000 and 55000, respectively Na-naphtalene sulfate, Na-lauryl sulfate, by means of the so-called “sacrificial anode method”.

Cyclic voltammetry has been applied to investigate the influence of the above mentioned stabilizers (type and concentration) on silver particles dimensions. The Ag concentration of the obtained colloidal solutions has been determined through UV-VIS spectra recording, involving a JASCO V 500 spectrophotometer. The nanoparticles sizes have been evaluated through DLS (Dynamic Light Scattering) technique involving Zetasizer Nano equipment and their morphology has been evidenced by TEM.

According to the obtained results, stable and high purity nano-Ag based colloidal solutions containing up to 35 ppm Ag and particles sizes around 10-20 nm have been electrochemically prepared. PVP stabiliser with co-stabilisers as Na-naphtalene-sulfonate, Na-lauryl sulfate, facilitates a suitable dispersion of nanoparticles and hinders their agglomeration. Zeta potential distribution is a monomodal one, with values between -18 ÷ - 30 mV that suggest the particles are covered by stabilizer and thus, the solution is stable.

## References

[1] J.H. Fendler, Nanoparticles and Nanostructured Films. Preparation, Characterization and Applications, Wiley-VCH, Weinheim, 1998.

[2] Bingsheng Yin, Houyi Ma,Shuyun Wang, J.Phys.Chem. B 107 (2003) 8898.

[3] W.C. Bell, M.L. Myrick J.Colloid. Interface Sci,, 242 ( 2001) 300.

# Nitrogenated nanocrystalline diamond, a new electrode material

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Diamond and diamond-based materials are extremely corrosion-resistant, have wide potential window and small background current; thus, they are perspective electrode materials. In this report, the electrochemistry of the nitrogenated nanocrystalline diamond thin-films will be discussed, with relation to their use as electrodes.

Nitrogenated nanocrystalline diamond films a few microns thick were grown on polished Si wafers as substrates, using microwave plasma CVD system operated at 2.45 GHz frequency, from the Ar-$CH_4$-$H_2$-$N_2$ gas mixtures. The $N_2$ content in the feeding gas was 0 to 25%. The films are characterized by AFM, SEM, Raman spectroscopy, electrical resistivity measurements. The electrodes were studied using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in solutions of indifferent electrolyte (2.5 M $H_2SO_4$) and $[Fe(CN)_6]^{3-/4-}$ redox couple. The potential window, background current, differential capacitance in the indifferent electrolyte, transfer coefficients and the CV current peak-to-peak potential difference $E_p$ in the redox solution are determined.

The nitrogenated nanocrystalline diamond electrodes showed good electrochemical properties. Like the boron-doped polycrystalline diamond electrodes, the nitrogenated nanocrystalline diamond electrodes demonstrated wide potential window (~2.1--3.4 V) and low background current (~10 μA/cm$^2$).

With the increase in the $N_2$ content in the feeding gas, the electrodes' differential capacitance increased, the electrode reaction in the $[Fe(CN)_6]^{3-/4-}$ redox system became more reversible. At 25% $N_2$ in the gas phase, the electrode behavior eventually approaches that of metal-like electrodes: $E_p$ approaches 60 mV, a "theoretical" value for reversible reactions.

Concerning the N content effect on their kinetic behavior, the nitrogenated nanocrystalline diamond electrodes qualitatively resembled nitrogenated amorphous carbon (a-C:N:H) electrodes; this enables us suggesting that the electrochemical behavior of the nitrogenated nanocrystalline diamond is determined by the N-containing amorphous carbon matrix (the intercrystalline boundaries), rather than the diamond nanosized crystallites proper.

The semiconductor properties of the nitrogenated nanocrystalline diamond electrodes are studied using a Mott--Schottky-plot approach; the conductance type, free carrier concentration and their mobility are estimated.

The nitrogenated nanocrystalline diamond is a promising electrode material for electrochemical applications.

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# Functional properties and topography of glucose biosensor based on poly(amidoamine) dendrimers.

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Glucose biosensors are the most widespread biosensing devices and they can be used not only for direct monitoring of glucose, but also for heavy metals detection by indirect monitoring of inhibition effect. We constructed glucose biosensor based on dendrimers – almost monodisperse macromolecules with regular and highly branch three-dimensional architecture, which increase the number of immobilized functional units. Their use in self-assembled monolayers of mixed alkanethiol-dendrimer layer on gold substrate is appropriate for enzyme immobilization.

The performance of the biosensor was detected amperometrically at 0.67 V vs. SCE and main functional characteristics were calculated. Individual layers of biosensors (hexadecanethiol (HDT); poly(amidoamine) dendrimers of first generation (G1); mixture of HDT+G1; glucose oxidase (GOX); and HDT+G1+GOX layers) were investigated by atomic force microscopy (AFM) to determine topography and effect of working potential and by cyclic voltammetry to determine integrity of the layers at presence of redox couple $Fe(CN)_6^{4-}$ / $Fe(CN)_6^{3-}$.

The AFM images were recorded both in air and in buffer environments, in tapping mode. We observed aggregates of G1 and GOX at gold surface in air, but not in buffer. The biosensor layer (HDT+G1+GOX) in air revealed smooth surface with irregular pinholes, but in the buffer the layer was corrugated. For the first time we investigated influence of dc voltage on the topography of sensor surface. We observed significant increase of the surface roughness after application of the potential 0.67 V to the biosensor layers during one hour, in comparison with layers without voltage application. The mechanisms of observed effects are discussed.

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# Gold Surfaces Modified with Enzyme Microstructures for Simultaneous Glucose and Glutamic Acid Monitoring

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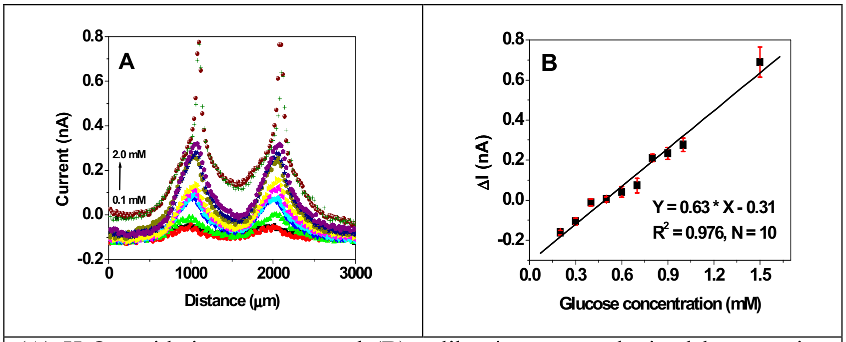
Mono- and bienzyme structures with typical dimensions of 100 µm were patterned on gold surfaces by shooting enzyme solution droplets of 100 pL, using a micro-dispensing system. The modified surfaces were analyzed by means of scanning electrochemical microscopy (SECM) operated in the generation-collection mode. The conversion of glucose and glutamic acid in the presence of glucose oxidase (GOx) and glutamate oxidase (GlOx), respectively, is accompanied by the generation of electrochemically active $H_2O_2$, rendering possible the determination of these compounds by using a Pt microelectrode polarized at +600 mV *vs.* Ag/AgCl (see figure below). Calibration curves for both glucose and glutamic acid were obtained with a good reproducibility by scanning the enzyme-modified surfaces. The main bioelectroanalytical parameters are presented in the table below.

| **Compound** | **Sensitivity (µA/M)** | **Detection limit (M)** | **Linear range (M)** |
|---|---|---|---|
| **Glucose** | 0.03 | $2.0*10^{-5}$ | $10^{-4}$ - $10^{-3}$ |
| **Glutamic acid** | 0.04 | $2.3*10^{-5}$ | $10^{-4}$ - $9*10^{-4}$ |



(**A**) $H_2O_2$ oxidation currents and (**B**) calibration curve obtained by scanning two GOx lines patterned on a gold surface. *Experimental conditions*: lines patterned from 20 mg/ml GOx, supporting electrolyte 0.1 M phosphate buffer with 0.1 M KCl (pH 7.2), $E_{app}$ = +600 mV *vs.* Ag/AgCl.

# Highly Active Carbon-Based Catalysts for Oxygen Reduction Reaction

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A major impediment to the commercialization of proton exchange membrane (PEM) fuel cells is the low activity of electrocatalysts for the oxygen reduction reaction. Platinum is considered the best cathode catalyst toward four-electron reduction of oxygen to water in acidic environments as it shows the lowest overpotential and the highest stability. However, Pt remains an expensive metal of low abundance, and it is thus of great importance to find Pt-free alternatives for PEM fuel cells.

In this work, a carbon-based electrocatalyst with high activity and selectivity was developed through carbon surface modification with different functional groups. The nano-sized transition metal was utilized as a catalyst for formation of nitrogen-rich active reaction sites for oxygen reduction. The number of the catalytic sites and the selectivity towards oxygen reduction to water were increased by optimizing oxygen functional group, nitrogen content, porosity, pyrolysis temperature, and chemical post-treatment. The optimized catalyst showed an onset potential for oxygen reduction as high as 0.87 V(NHE) in $H_2SO_4$ solution which is comparable to that of a conventional Pt catalyst. The catalyst produced no hydrogen peroxide ($H_2O_2$) during oxygen reduction in comparison with 1 to 2 % $H_2O_2$ on a platinum catalyst. The fuel cell test showed the current densities of 1.1 A cm$^{-2}$ at 0.4 V and 2.3 A cm$^{-2}$ at 0.2 V for a catalyst loading of 6 mg cm$^{-2}$. Further, the catalyst exhibited no degradation of fuel cell performance for 350 h of continuous operation.

# Modelling of non-linear reaction-diffusion processes of amperometric polymer-modified electrode

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A mathematical model of amperometric response for a polymer-modified electrode system has been developed. The model is based on non-stationary diffusion equations containing a non-linear term related to Michaelis-Menten kinetics of the enzymatic reaction. In particular, the interplay between chemical reaction and substrate diffusion is specifically taken into account. The limiting situations of catalytic site unsaturation and site saturation are considered. The analytical solutions for substrate concentration and transient current for both steady and non steady state are obtained using Danckwerts' relation and variable and separable method. An excellent agreement with the previous analytical results are noted.

**Keywords**: Modelling ; Reaction-diffusion; Non-linear; Polymer-modified electrodes; Michaelis-Menten kinetics.

# Electrocatalytic Oxidation and Voltammetric Determination of Sulfite at the Surface of Carbon Paste Electrode Spiked With a New Ferrocene Derivative

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Sulfites are commonly used in the food and pharmaceutical industries as preservatives and antioxidants and brewing industry as an antibacterial agent. Despite these grate advantages, the sulfite content in foods and beverages should be strictly limited due to its potential toxicity and products containing more than the established threshold level must be adequately labeled [1]. In large quantities, sulfite and its oxidation products are pollutants. It has been demonstrated that sulfite can undergo catalytic or mediated oxidation using some chemically modified electrodes (CMEs) [2-5].

In this work, a chemically modified carbon paste electrode with 2, 7-bis (ferrocenyl ethyl) fluoren-9-one (2, 7-BFEFMCPE) was employed to study the electrocatalytic oxidation of sulfite in aqueous solution using cyclic voltammetry, differential pulse voltammetry and chronoamperometry. It has been found that under optimum condition (pH 8.00) in cyclic voltammetry, the oxidation of sulfite occurred at a potential about 420 mV less positive than that unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, α and catalytic reaction rate constant, $K'_h$ were also determined using electrochemical approaches. The electrocatalytic oxidation peak current of sulfite shows a linear calibration curve were obtained in the range $8.7\times10^{-5}$ M - $1.1\times10^{-2}$ M and $4.0\times10^{-6}$ M – $4.43\times10^{-4}$ M of sulfite concentration with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods respectively. The detection limit (2δ) was determined as $5.3\times10^{-6}$ M and $2.1\times10^{-7}$ M by CV and DPV methods. This method was also examined as a selective, simple and precise new method for voltammetric determination of sulfite in real sample.

## References

[1] L. G. Decnopweever and J. C. Kraak, Anal. Chim. Acta 337 (1997) 125.
[2] I. G. Casclla, R. Marches, Anal. Chim. Acta 311 (1995) 199.
[3] N. Ekkad, C. O. Huber, Anal. Chim. Acta 332 (1996) 155.
[4] X. Su, W. Wei, L. Nei, S. Yao, Analyst 123 (1998), 221.
[5] R. Ojani, J. B. Raoof, A. Alinazhad, Electroanalysis *14* (2002) 1197.

# Electrocatalytic Determination of L-Cysteine at the Surface of Ferrocenedicarboxylic Acid Modified Carbon Paste Electrode

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L-cysteine and its derivatives have attracted especial attention because of its involvement in many important biological processes, and its chemical activity in the formation of complexes with various ionic species and biomolecules [1]. L-cysteine is a highly significant bioactive compound, and is known to be an active site in the catalytic function of certain enzymes known as cysteine proteases and in many other peptides and proteins. It is also used in some proprietary antibiotic preparations used for the treatment of skin damages and as a radioprotective agent [2, 3]. Therefore, investigation of the electrochemical behavior of L-cysteine and its determination via a simple and reliable method is of great importance [4, 5].

In this work, the electrochemical behavior of L-cysteine studied at the surface of ferrocenedicarboxylic acid modified carbon paste electrode (FDCMCPE) in aqueous media using cyclic voltammetry, differential pulse voltammetry and double potential step chronoamperometry. It has been found that under optimum condition (pH 8.00) in cyclic voltammetry, the oxidation of L-cysteine occurs at a potential about 200 mV less positive than that of an unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, $\alpha$ and catalytic reaction rate constant, $k_h$ were also determined using electrochemical approaches. The electrocatalytic oxidation peak current of L-cysteine showed a linear dependent on the L-cysteine concentration and linear analytical curves were obtained in the ranges of $3.0\times10^{-5}$ M–$2.2\times10^{-3}$ M and $1.5\times10^{-5}$ M–$3.2\times10^{-3}$ M of L-cysteine concentration with cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods respectively. The detection limits ($2\delta$) were determined as $1.7\times10^{-5}$ M and $9.9\times10^{-6}$ M by CV and DPV methods. This method was also used for the determination of L-cysteine in some pharmaceutical samples, such as acetylcysteine tablets and aminoplasma serum by using a standard addition method.

**References**

[1] B. Yosypchuk, I. Novotny, Talanta 56 (2002) 971.
[2] J. Kulys, A. Drungiliene, Anal. Chim. Acta 243 (1991) 287.
[3] S. A. Wring, J. P. Hart, B. J. Birch, Analyst 114 (1989) 1571.
[4] J.B. Raoof, R. Ojani and M. Kolbadinezhad, Electroanalysis 17 (2005) 2043.
[5] J.B. Raoof, R. Ojani, Hadi Beitollahi, R. Hossienzadeh, Anal. Sci., 22 (2006) 1213.

# GRAVI-Chips: Disposable Nanofluidic Electrochemical Cells for Fast Analysis

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DiagnoSwiss has developed an electrochemical microchip technology dedicated to ultra-fast analysis in low sample volume. To this end, the developed chips comprise a series of electrochemical cells consisting of an array of sub-microfluidic channels. If desired, these sensors can work in parallel, and they have been designed to be compatible with portable, bench-top as well as high-throughput instrumentation.

These microchannel arrays with embedded microelectrodes called GRAVI-Chips are fabricated in large volume thanks to a printed circuit board technology using deep plasma etching.[1] Different applications have been shown with these platforms such as enzyme-linked immunosorbent assays (ELISA) for the detection of interleukin, hormone and vitamin for instance. [2-3]

In this presentation, we will show the GRAVI-Chip concept in which pump-less analysis can be carried out in very short time and with minimum manual handling. The use of these electrochemical cells will be illustrated by example of application such as the detection of cytokines by ELISA.

Examples of the application of the GRAVI-Chip platform for heavy metal analysis or cell culture monitoring will also be presented and will illustrate how these nanofluidic electrochemical cells enable to reduce the time to results and the analyte/sample consumption.

*Acknowledgment: DiagnoSwiss thanks the European Commission for financial support of part of this work (NeuroTAS project Nr LSHB-CT-2006-037953).*

*[1] Rossier JS., Vollet C, Carnal A, Lagger G, Gobry V, Girault HH, Michel P, Reymond F; Lab Chip, 2002, 2:145-150.*

*[2] Hoegger, D.; Morier, P., Vollet P, Heini, D, Reymond, F. and Rossier JS; Disposable Microfluidic ELISA for the Rapid Determination of Folic Acid Content in Food Products; Analytical and Bioanalytical Chemistry; in press.*

*[3] Morier P, Vollet C, Michel PE, Reymond F, Rossier J.S.; Electrophoresis, 2004, 25:3761-3768.*

# Electrochemical synthesis of nanoparticles: nucleation, growth and ultrasonic detachment

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The synthesis of nanoparticles has attracted considerable attention in recent years due to their many applications. A central problem for the widespread use of these materials in nanoscale devices and in applications e.g., optical detection in bioanalysis, requires accurate control of size and, importantly, geometry. The latter is particularly important for electromagnetic enhancement, for instance, for their use in Surface Enhanced Raman Spectroscopy. Electrodeposition offers an attractive way for nanoparticle synthesis since the applied potential can be used for the control of nucleation and growth of metal clusters at the electrode surface. The present work describes attempts to control silver nanoparticle synthesis by the independent control of the heterogeneous nucleation of metal clusters (seed control) followed by growth by electrodeposition on these nuclei (electrochemical growth), with the synthesis cycle terminated by nanoparticle dislodgement by an ultrasound pulse. The formation of stable nanoparticles by this method has been demonstrated by UV-vis spectroscopy and TEM imaging of the preparations obtained. Partial size separation has been achieved by centrifugation of the dispersion prepared.

# Electroless deposition of nanotubes.

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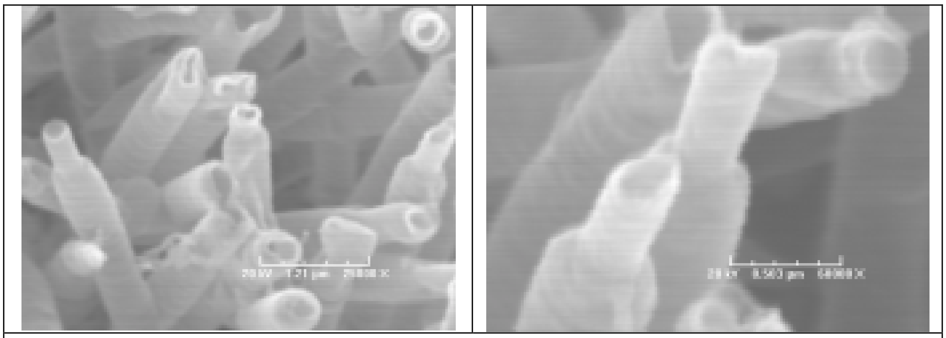
Nanostructured metal deposits have potential applications in various technologies based on their electrical, catalytic, magnetic or other properties. Nanostructuring of metals and alloys is possible using template materials such as anodised aluminium oxide (AAO) or polycarbonate (PC) track etched polymers. Deposition processes that may be utilised to achieve the nanostructured materials include electrolytic and chemical vapour deposition. An alternative low cost process is electroless deposition which facilitates the deposition of a wide range of materials. Reducing agents (hypophosphite, boranes, formaldehyde or borohydride) provide the electrons to achieve deposition. Boranes are active reducing agents which may yield up to six electrons per molecule. [1,2] Because they may be oxidised on a wide range of metals they may deposit on various substrates and deposit many technologically important materials. Previous work has shown the electroless deposition of single metal nanotubes using formaldehyde or hypophosphite reducing agents. In this work we investigate the template assisted electroless deposition of a number of metals and alloys resulting in metal or alloy nanotubes and coaxial metal nanotubes using borane reducing agents. The processing requires sensitisation of the substrate followed by catalyst activation and finally metal deposition at 50 to 85$^{o}$C. The process deposits ~50nm of the first metal or alloy on the catalysed sidewall of the nanotemplate and this is followed by a second metal or alloy deposition ~50nm on the inner wall of the templated metal. The analysis to be presented will include TEM, SEM, EDX, XRD, and electrochemical data.



Coaxial nanotubes of nickel and cobalt deposited by electroless deposition.

1. L.C.Nagle and J.F.Rohan, Electrochemical and Solid-State Letters, 8 (5) C77-C80 (2005)
2. L.C.Nagle and J.F.Rohan, Journal of the Electrochemical Society, 153 (11) C773-C776 (2006)

# Stability of Substituted 4-Bromobenzene and 4-Nitrobenzene Groups Electrochemically Grafted at Carbon Electrode Surface

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The electrochemical reduction of an aryl diazonium tetrafluoroborate salt, dissolved in acetonitrile, at a carbon electrode surface allowed the grafting of aryl groups with the formation of a carbon- carbon bond. Groups such as 4-nitrobenzene and 4-bromo benzene were grafted at a glassy carbon electrode surface. The stability of these grafted groups, present at the glassy carbon electrode surface, was studied at various electrode potentials in aqueous media. In appropriate experimental conditions, the as-grafted groups severely inhibit the cyclic voltammetry response of selected redox probes. Thus, the reappearance and /or increase of an electrochemical response, after polarization, were taken as an indication that a modification of the grafted layer occurred. The results of this work demonstrated that polarization at very positive (ca.1.8V) and negative (ca.-2V) potential is needed to observe and electrochemical response. Electrochemical impedance spectroscopy was also used to investigate the stability of the grafted layers. The impedance data usually tracks fairly well the cyclic voltammetry results, although the former appears to be more sensitive to changes that are occurring upon polarization of the modified electrode.

## REFERENCES

[1]. J. Liu, L. Cheng, B. Liu and S. Dong, Langmuir.,16,7471,(2000).
[2]. Abbas A. Rostami and Mark T. McDermott, e-Journal of Surface Science and Nanotechnology, 4, 419,(2006).

Keywords: Modified electrode, Diazonium salts

# *In-situ* Synchrotron X-ray Absorption Studies of Electrochemically Deposited ZnO Nanostructures

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ZnO nanostructures have great promise in a wide range of applications such as sensors, optoelectronics, piezoelectronics *etc*. Preparation of oxide films by electrodeposition from aqueous solution presents several advantages over other techniques such as controlling the rate and morphology through well-defined parameters (electrode potential, current, temperature, pH, etc.), electrolytic processing is a well-established technology and readily scalable for production, and the non-equilibrium nature of the electrochemical interface often gives rise to morphologies and compositions not attainable via other, usually high-temperature, routes.

The mechanism of nanostructured ZnO nucleation and growth under electrochemical conditions is not well-understood, and is a key factor for the control of the morphology, and properties of the films. We will discus the use of *in-situ* synchrotron x-ray absorption spectroscopy during film deposition to elucidate these factors. Since it is species-specific this approach allows the film growth to be directly correlated with the electrochemistry. We have found that the deposition rate vs. time curve contains distinct regions corresponding to nucleation, 1d growth and (sometimes) bulk-like growth. The nucleation step is particularly potential dependent with near-instantaneous nucleation at very low potential (-0.85 $V_{she}$) but longer nucleation time at less negative potentials (e.g. -0.65 $V_{she}$). One effect of this is a different size dispersion of the nano-structured material as a function of the deposition potential.

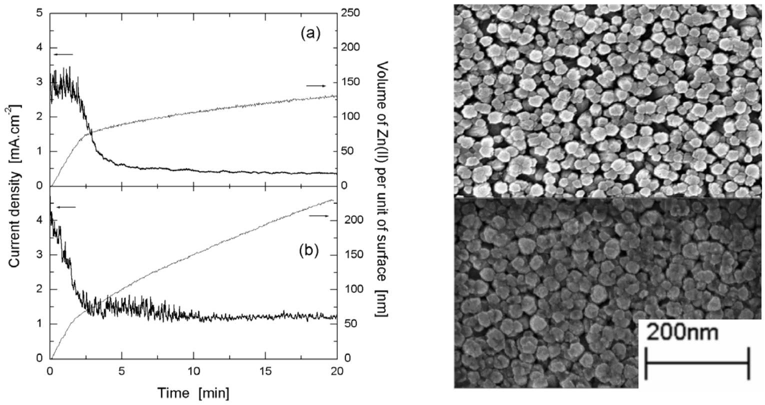

Figure 1. Deposition rate from XAS compared to the electrochemical current transient (left) and corresponding microstructures deposited from a 5 mM $ZnNO_3$ bath at 70ºC. [top -0.65 Vshe, bottom -0.85 Vshe]

# Electrochemical Preparation of an Ideally-Structured Porous Silicon Rugate Filter

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## Introduction

Porous silicon rugate filters (PSRFs) are characterized by sinusoidal variation of refractive index in the direction perpendicular to the surface, which produces a kind of 1-D photonic structure. The filters can be used for sensing chemical and biochemical species. In the electrochemical design of a PSRF, it is generally assumed that the sinusoidal variation of the etching current with time maps to the corresponding sinusoidal change of refractive index with depth because porosity and therefore refractive index of the formed porous layer vary with current density. This assumption is reasonable as long as the etching rate is constant irrespective of applied current density. Herein, we investigate the dependence of etching velocity on current density and its related effects that should be taken into consideration for accurate PSRF design.

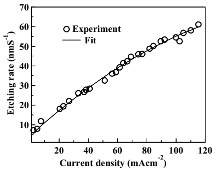

**Fig. 1 Etching rate of silicon as a function of current density.**

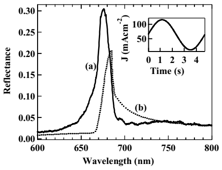

**Fig. 2 Measured (a) and calculated (b) spectra for a 100-cycle PSRF formed by a sinusoidal current density waveform shown in the inset.**

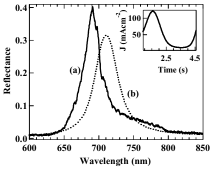

**Fig. 3 Measured (a) and calculated (b) spectra for a 100-cycle PSRF formed by a modified sinusoidal current density shown in the inset .**

## Results and Discussion

Several porous silicon layers were formed by electrochemical anodization of boron-doped p-type (100) silicon wafer (3.2-4.8 Ω cm) in a 1:0.6 (v/v) solution of 49% aqueous hydrofluoric acid and ethanol at various current densities. Accurate estimation of the etch rates and refractive indices is performed. The etching rate rises steadily as current density increases as displayed in Fig.1. The refractive index of the individual porous silicon layers was estimated from its reflectance spectrum. A PSRF was prepared in the same HF solution using a sinusoidal current density oscillating between 115.3 and 10.2 mAcm$^{-2}$. Following the calibration curves of the etching rate and refractive index, the resulting refractive index profile was found to have a deformed sinusoidal shape. Fig. 2 shows a good agreement between the experimental reflectance spectrum and that calculated using the deformed refractive index profile. The etching current density was modified as shown in the inset of Fig. 3 to produce a sinusoidal variation of refractive index. The recorded reflectace spectrum of this structure matches its simulated one better than the case of Fig. 2.

# Fluorescent films of dansyl derivatives: preparation, voltammetric and AFM characterization

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Electrochemical properties of supramolecular systems have been hardly investigated in this new century, mainly due potential application for design of molecular-level devices. Dansyl group shows intense absorption bands in the near UV and a strong yellow-green fluorescence in the visible region being extensively used for sensing or labelling purposes in supramolecular systems [1]. Dansyl-based fluorescent films were prepared by chemical and electrochemical methods and its electrochemical and morphological properties were investigated. The electrodeposited DNS-gly film, which presented greater surface roughness (Fig. 1A) and larger relative surface area in comparison with its chitosan dansyl analogous (Fig. 1B), exhibited better electrochemical response when investigated by cyclic voltammetry (CV, Fig. 2). This behaviour can be attributed to the higher number of active sites present in the well-organized structure of the electrodeposited film in comparison with the chemically produced film.

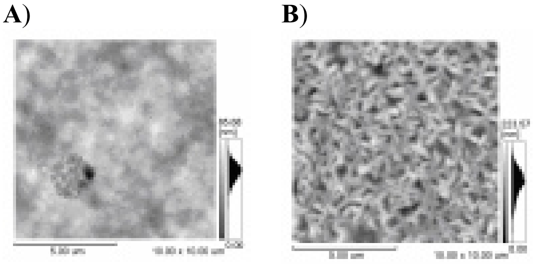

Fig. 1. Two-dimensional AFM images of films of (**A**) DNS-chitosan and (**B**) DNS-gly deposited on ITO.

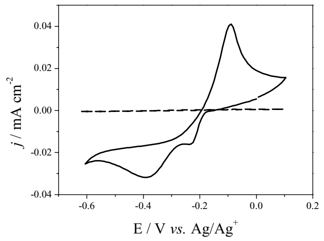

Fig. 2. CV of DNS-chitosan (---) and DNS-gly (—) films, in $LiClO_4/CH_3CN$ 0.1 molL$^{-1}$, $\nu = 20$ mVs$^{-1}$.

Films employing the dansyl group as sensing agent exhibit two fundamental characteristics, namely, electrical conductivity and visible light fluorescence. These films offers promising technological application in, for example, devices with electric activity/conductivity as LEDs or sensors.

[1] P. Ceroni, I. Laghi, M.Maestri, V. Balzani, S. Gestermann, M. Gorkab, F.Vogtle, New J. Chem. 26 (2002) 66.

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# Synthesis and Characterization of Polyaniline-Sulfonated Phthalocyanine Thin Films

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Aniline was polymerized electrochemically in acidic electrolyte in the presence of tetrasulfonated nickel phthalocyanine. It was observed that the polymerization rate is significantly accelerated by the phthalocyanine and the latter is incorporated into the growing film to form a composite material. Thus formed composite was characterized by cyclic voltammetry, UV-vis spectroscopy and AFM.

Cyclic voltammograms of the polyaniline-phthalocyanine showed several couples of peaks. Some of them were assigned to polyaniline and the others to reversible reduction-oxidation of phthalocyanine ligand. Unlike pristine polyaniline, the composite studied here showed its electrochemical activity in a broad pH range (up to 9). This is due to the incorporation of sulfonated macromolecules which act as a co-dopands and are not realised from the film bulk upon reversible potential cycling. Moreover the composite films showed electrocatalytic activity toward the oxidation of ascorbic acid in neutral phosphate buffer.

UV-vis spectra of the composite film deposited on a conducting glass slides showed features characteristic of both polyaniline and phthalocyanine confirming successful incorporation of phthalocyanine molecules into growing polyaniline and the composite film appeared to be electrochromic. The colour changed from light pink to green, blue and dark blue as the electrodic potential was raised.

Surface analysis by AFM showed globular structures uniformly distributed over the film which presumably belong to aggregates of phtalocyanine molecules.

The composite studied in this work could be applied as ascorbic acid or pH sensor as well as electrochromic material for optoelectronic applications.

# Simulation of the cathodic delamination process of coatings on metal surfaces

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The finite element method (FEM) is well known in the engineering technology. In this work we will show the applicability of this powerful tool to an important electrochemical problem in corrosion research, namely the simulation of the process of delamination of polymer coatings from metal substrates.

In a first step, the mathematical equations are generalized to handle flexibly different electrochemical mechanisms and electrode geometries. Then a numerical method was developed for predicting current density and potential distribution in electrochemical systems. The fundamental transport equation consists of a partial differential equation (PDE) involving linear and non linear terms of diffusion convection and migration of species. The boundary Conditions (BCs) are described by PDE including flux conditions.

Since a major problem of simulating delamination is the lack of knowledge of how to describe the diffusion and migration at the interface, the kinetics of the electrochemical reactions (esp. oxygen reduction) at the buried interface and the degradation caused by oxygen reduction were measured on precisely defined model systems. The parameter set obtained from this experiment was used as a basis for the simulations.

# Electrosynthesis of Ni/Al-hydrotalcite: study of the growth on electrode surface

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Hydrotalcite-like compounds (HTs) are bidimensional nanostructured materials consisting of positively charged brucite-like layers; electroneutrality is achieved by intercalation of anions in the interlayer spaces. Their general formula is $[M_a(II)_{1-x} M_b(III)_x(OH)_2]^{x+}(A^{n-}{}_{x/n})$ $mH_2O$, shortly named $M_a/M_b$-A, where $M_a$ and $M_b$ are a bivalent and a trivalent metal, A is the anion and x ranges between 0.17 and 0.44. In case $M_a$ is a transition metal, like Ni or Co, the HT displays improved charge transport properties.

Materials belonging to this family have many potential applications, such as precursors for coatings and catalysts and anion exchangers. Moreover, they are widely employed as modifiers for electrochemical surfaces in the development of ion selective electrodes or amperometric sensors. Recently, HTs have also been proposed as matrices for enzyme immobilization in the development of amperometric biosensors. Most of the aforementioned applications require HT films of controlled thickness to be deposited.

A study was performed to find the best experimental conditions to obtain thin and homogeneous films of a Ni/Al-$NO_3$ HT by electrosynthesis on a platinum electrode surface. Experiments were carried out by application of a cathodic potential, for a fixed time, to a Pt electrode soaked in a 0.3 M $KNO_3$ solution containing Ni and Al (molar ratio 3:1). Two different metal concentrations were investigated. The films were characterized by SEM-EDS, AFM and SECM.

When the more concentrated solution was employed, the coverage of the electrode surface increased with the electrosynthesis time and the films were not uniform, displaying zones with different thickness. The composition was in agreement with that of a Ni/Al-$NO_3$ HT only for very high deposition times. EDS analysis let us to draw some conclusions about the mechanism of film growth: $Al(OH)_3$ was formed at first, then the further increase of pH, due to nitrate reduction, resulted in the dissolution of the hydroxide, which, in the presence of $Ni^{2+}$, converted to Ni/Al-$NO_3$ HT.

As regards the more diluted solution, thin, homogeneous and continuous films of pure HT was obtained even at short times. The Ni/Al ratio of the electrosynthesised material was 2:1, compatible with the value expected for a HT phase. In such a case the mechanism of film growth is probably different, since the direct precipitation of the HT on the electrode occurs. Electrochemical behaviour of all the modified electrodes was checked by cyclic voltammetry in basic solution and by AC impedance spectroscopy; evidencing that electron transfer resistance is mostly affected by the electrodeposition time, i.e. the film thickness. The best electrosynthesis conditions were employed for immobilizing glucose oxidase and the response of the biosensors (in terms of sensitivity, selectivity and lifetime) was studied.

# Lipopeptide Nanopores As Voltage Sensors In Planar Lipid Bilayers

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Artificial lipid bilayers are the useful tool in studying both the lamellar lipid structures and proteins, associated with the cellular membranes. Stable ion-permeable nanopores of ~2 nm in diameter, produced by cyclic lipopeptides (syringomycin E, syringopeptin E, syringopeptin A, syringostatin A, and syringotoxin B) in the lipid bilayers are highly sensitive to the voltage applied across these bilayers, as well as on its surface and inner (dipole) potential. The nanopores are spontaneously formed upon one-side addition of the above lipopeptides to the bilayer lipid membranes and application of the external voltage. Single lipopeptide nanopores are associated into clusters, possessing different degrees of the pore conductance synchronization. The number of the clustered nanopores depends on the external voltage. Varying the bilayer surface charge by admixing different portions of the negatively charged lipids in the membrane-forming mixture affects reproducibly the ion conductance of the single nanopore and the polarity of the transbilayer voltage that stimulates pores opening. More important, the nanopore properties are determined by the dipole potential of the bilayer. Decrease of the bilayer dipole potential reduces elementary pore ion conductance and increases the degree of pore association in the cluster. At the same time the voltage sensitivity of the pore formation decreases.

Overall, we suggest the lipopetide pores as promising nano-sensors, able to probe essential characteristics of the lipid bilayers.

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# THIN LAYER ELECTROLYTIC $Co_9S_8$ FOR LITHIUM POWER SOURCES

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Since transition metal oxides were envisaged in 2000 by Tarascon's group as active materials for the negative electrode of lithium–ion batteries, extensive work was also carried out with different transition metal compounds (mostly oxides, in which the transition metal is at low oxidation state). Ni and Co sulfides may be also of special interest. The synthetic modes of these compounds define considerably their electrochemical properties. It has been shown by us that nano-sized electrode materials, such as Co and Ni oxides can be synthesized by electrolysis. Satisfactory electrochemical performance of electrolytic Co sulfides in lithium cells was obtained. In this case, the electrolytic product contains a few Co sulfide compounds ($Co_9S_8$, $Co_3S_4$, $Co_4S_3$, CoS, etc.) Production of electrolytic single Co sulfide compound and its optimization in lithium test cells is our further investigation task. The aim of this communication is to show some results about the synthesis and evaluated properties of such single Co sulfide.

Thin film deposits have been produced on Al-foil by cathodic reduction of water solutions comprising Co-sulfate and thiosulfate ions. XRD patterns of the film correspond to the characteristics of $Co_9S_8$ at unavailability of other compounds reflexes. The images of $Co_9S_8$ deposits in HR-SEM show nanostructure formation in which minimum grain size is about 23 nm. By differential capacity–potential to $Li/Li^+$ data of $Co_9S_8$ electrode it is the evidence of its stable reversibility during 10 cycles (Fig. 1). After the first cycle, electrochemical process is repeated with the regularity having a pair of redox cathodic and one anodic transitions.

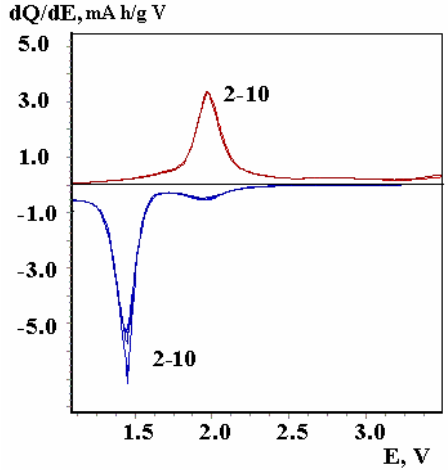

Figure 1. Differential capacity–potential curves of a thin film $Co_9S_8$ electrode in EC - DMC/ $LiClO_4$ solution.

# Evaluation of activated 4-nitrothiophenol modified Au electrodes as potential interface for biosensing applications

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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 (4-NTP) monolayers on the Au electrode surfaces have been evaluated. Following chemisorption of 4-NTP on Au surfaces under formation of a dense self-assembled monolayer, the conversion of the nitro groups to hydroxylamine intermediates by electrochemical reduction was studied at different conditioning potentials using cyclic voltammetry. At a pH-value of 8 for example, the nitrothiophenol monolayer can be efficiently and selectively converted into the hydroxylamine terminated one at a potential of -470 mV *vs*. Ag/AgCl. The full reduction to aminothiophenol can be avoided by choosing the appropriate conditioning potential.

$$\text{Au-S-C}_6\text{H}_4\text{-NO}_2 + 4\text{H}^+ + 4\text{e}^- \longrightarrow \text{Au-S-C}_6\text{H}_4\text{-NHOH} + \text{H}_2\text{O}$$

$$\text{Au-S-C}_6\text{H}_4\text{-NO} + 2\text{e}^- + 2\text{H}^+ \rightleftarrows \text{Au-S-C}_6\text{H}_4\text{-NHOH}$$

$$\text{Au-S-C}_6\text{H}_4\text{-NHOH} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{Au-S-C}_6\text{H}_4\text{-NH}_2 + \text{H}_2\text{O}$$

Despite the observed poor stability over time the nitroso/hydroxylamine redox couple could be easily reactivated by conditioning at the appropriate potential. The monolayer modified Au electrode exhibited electrocatalytic properties especially for electron transfer reaction with 2-electron transfer mediators.
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 to the working electrode generated local modifications of the redox state of the monolayer headgroups. By means of SECM in the feedback mode in the presence of a suitable free-diffusing redox mediator the redox state of the surface bound species can be visualized ("reading").
Oxidation of NADH at locally activated 4-NTP monolayers is investigated and first results concerning dehydrogenase based amperometric biosensors using locally activated monolayers will be described.

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

# Composite materials based on polythiophenes and metal nanoparticles

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Conducting polymers are widely employed as electrode coatings, aiming at improving the electrocatalytic capability and inducing antifouling effects. A step forward consists in the preparation of composites including metal functionalities inside the polymeric matrix, in order to further increase the electrocatalytic performance. In particular, inclusion of noble metal nanoparticles, whose catalytic properties are well known and that are widely exploited in a variety of applications, constitutes one of the most interesting possibilities. In this frame, composite materials based on polythiophenes are far from being exhaustively investigated.

Our recent and present research activity is carried out along such a line. In particular, we synthesised Au and Pt nanoparticles with size ranging from 2 to 15 nm, encapsulated by citrate, tannic acid, 3,4-ethylenedioxythiophene and different tetraalkylammonium salts, i.e. bearing neutral and charged moieties. The resulting nanoparticle systems have been characterised by the most suitable spectroscopic and microscopic techniques, such as XRD, TEM-EDS, NMR, IR, UV. Different procedures have been followed in order to include the nanoparticles inside different polymeric matrices based on polythiophenes. The first strategy has involved the electropolymerisation of a series of both commercial or originally synthesised monomers, bearing different functional groups capable of anchoring metal nanoparticles. The composites have been formed by electropolymerisation in solutions containing both the monomer units and the nanoparticles. Alternatively, the same monomers have been employed for the electrogeneration of electrode coatings in the absence of the nanoparticles; afterwards, the nanoparticles have been anchored on the surface of the coating by simply dipping the coated electrode into a solution containing the nanoparticles. Finally, polymers bearing charged functionalities have chemically synthesised starting from monomers possessing ionic groups; composites have been assembled on the electrode surface by means of the layer-by-layer technique.

The composites formed on the electrode have been characterised by TEM-EDS, XRD, SEM, ICP, electrochemical and spectroelectrochemical techniques. In view of the applications in amperometric sensors, the electrochemical behaviour with respect to different kinds of benchmark electroactive species, such as ascorbic acid, dopamine, paracetamol, methanol and glucose, has been tested by voltammetric techniques. It was possible to induce selectivity to the electrochemical device, by suitably changing the experimental conditions. As an example, encapsulating species functionalised with ionic moieties activate a sort electrostatic shield: the access of charged electroactive species to the redox active centres on the electrode can be modulated by changing the charged residues on the encapsulating agent.

# Ionic transport studies on conductivity behaviour of polymer electrolytes containing $NH_4PF_6$

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The effect of addition of propylene carbonate (PC) and nano size fumed silica on the conductivity behaviour of polyethylene oxide (PEO) based polymer electrolytes containing ammonium hexafluorophosphate ($NH_4PF_6$) has been studied. Polymer electrolytes containing both PC as well as fumed silica show maximum conductivity alongwith an improvement in mechanical properties. The formation of ion aggregates at higher concentrations of salt and their dissociation with the addition of PC has been supported by FTIR studies. X-ray diffraction studies show the presence of crystalline/amorphous phases in different electrolytes. The addition of fumed silica has been found to improve the thermal stability of polymer electrolytes and are found to be thermally stable upto 125 °C. Line narrowing observed in the variation of $^1H$ and $^{19}F$ NMR linewidth with temperature suggests that both cations and anions are mobile in these polymer electrolytes. Different ion transport parameters such as jump frequency, diffusion coefficient etc. have also been calculated from NMR data and their variation with temperature has been correlated with the conductivity results. The morphology of different polymer electrolytes has been studied by SEM.

# Supercapacitor Electrode from Carbon Fiber/Conducting Polymer Nano-Composites

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The nano-thin PPy layers deposited on to the highly conductive carbon substrate of the vapor grown carbon fibers (VGCF) was aimed to understand some details of pseudo-capacitive behavior of the PPy. Using different concentrations of the pyrrole, could control the thicknesses of deposited PPy layers. Surface morphology and thickness of the deposited PPy layers were confirmed by means of scanning electron microscopy (SEM) and scanning transmission emission microscopy (TEM). Pseudo-capacitive behavior of the deposited PPy layers on VGCF investigated by means of cyclic voltammetry. Then, the PPy/VGCF composites were mixed with activated carbons (AC) at various mixing ratios. For the PPy/VGCF/AC composite electrodes, characteristics of specific capacitance and power capability were examined by half-cell tests. As results of this study, it was investigated that nano-thin PPy layer below ~10 nm deposited on VGCF had high pseudo-capacitance and fast reversibility. Its specific capacitance per averaged weight of active material (PPy) was obtained as ~588Fg$^{-1}$ at 30mVs$^{-1}$ and maintained as ~550Fg$^{-1}$ at 200mVs$^{-1}$ of scan rate. Also, from the mixing 60 wt.% of the PPy/VGCF with 25 wt.% of AC, the PPy/VGCF/AC composite electrode exhibited higher power capability maintaining the specific capacitance per active materials of PPy and AC as ~300Fg$^{-1}$ at 200mVs$^{-1}$ in 6M KOH.

Keywords: Pseudo-capacitance; Electric double layer capacitance; Composite electrode; Supercapacitor

References:
[1] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J. Power Sources 1994, **47**, 89.
[2] C.C. Hu, X.X. Lin, J. Electrochem. Soc. 2002, **149**, A1049.
[3] Y.C. Liu, C.J. Tsai, Chem. Mater. 2003, **15** 320.
[4] M.D. Ingram, H. Staesche, K.S. Ryder, Solid State Ionics 2004, **169** 51.

# Interface Resistance Between Nanostructured Thin Layers of Electrochemicaly Active Materials and Metallic Substrate

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The value of contact resistance between the nanostructured thin layer electrode material and metallic current lead is among the key parameters of energy storage devices: batteries, supercapacitors, sensors, solar cells, etc.

This resistance is a function of the ohmic contact that is determined by the micro relief of the deposited surface, as well as by the availability and the total surface area of the insulating passivation film that is formed on the surface of the current lead.

Authors of the paper developed and presented the method and an eddy current system for non-contact evaluation of the resistance between the coating and current lead stripe during continuous fabrication of electrodes for chemical power sources, for example lithium batteries, supercapacitors, sensors, solar cell, etc.

In paper will be presented results of the investigation of structure, interface resistance and electrochemical properties the nanostructures thin film electrodes which have been obtained based on different vacuum deposition technologies and apparatuses.

Combination of developed non-contact electromagnetic method and the fuzzy logic systems provides improvement in the properties of produced electrodes and allows to realize the higher stability action of complicated factor and to increase the reliability of testing and control in comparison with traditional system.

References:

1. “Eddy-current method and system of non-contact evaluation of resistance” V. Redko et all. PCT/UA2006/000038 of 13.06.2006
2. “Fuzzy Logic”. V. Khandetskyy, V. Redko, T. Pastushkin, P. DNU, 2005.-230 p.

# Electrodeposition of Gold and Silver Nanoparticles of Controlled Size and Interparticle Spacing: Application to Single Nanoparticle SERS

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Noble-metal nanoparticle arrays can be used to perform surface enhanced Raman scattering (SERS), producing enhancement factors of up to $10^6$. This dramatic effect results from enhancement of the electromagnetic field surrounding the nanoparticles by resonant excitation of the surface plasmon band. Isolated noble-metal nanoparticles have the further advantages over arrays such as compactness and precision of placement. Electrodeposition is chosen to produce these surfaces because it affords the ability to control the driving force behind the electrochemical growth of nanostructures, and accordingly control the physical properties of the resulting deposits such as particle size and interparticle spacing. In addition electrodeposited nanoparticles are more strongly bound to the underlying surface compared to chemically linked nanoparticles. A method for the electrodeposition of noble-metal nanoparticles with controlled nanoparticle size is presented. The tuning of arrays to maximize sensitivity by altering individual particle size and interparticle spacing is also presented.

Fluorine doped tin oxide (FDTO) is chosen as the metal nanoparticle substrate for its ability to conduct charge along with its optical clarity to visible wavelengths. Metal nanoparticles are electrodeposited onto FDTO using the two pulse method: A large overpotential pulse of short duration is initially applied to create nucleation sites for nanoparticle growth on the FDTO surface; subsequently, a second, lesser overpotential is applied and maintained to facilitate particle growth from the nuclei. The overpotential and duration of the pulses are controlled such that the desired nanoparticle size and interparticle density are achieved. The size and density of nanoparticles is confirmed by scanning electron microscopy. Finally, SER spectra of either a probe molecule monolayer, or a physiologically significant analyte such as a peptide, are acquired to assess the effectiveness of the single and arrayed nanoparticles.

The SERS arrays and single nanoparticles have the potential to be incorporated into high sensitivity diagnostic sensors for the detection of trace analytes. The nature of the substrate used, fluorine-doped tin-oxide, makes it possible that these sensing platforms can be produced inexpensively and quickly, so that they could be used as a disposable, single use platform for detection.

# Synthesis and Characterization of Peo Blend P(Tmc) Solid Polymer Electrolyte

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Since Wright et al. First reported the ionic conduction of poly(ethylene oxide) (PEO) and alkali metal salt complexes in 1973 [1], the study of ion transport mechanism and the development of materials have been extensively investigated due to their potential applicationns such as high-energy density rechargeable batteries, electrochromic display, ion sensors, and so on [2,3]. The results of the characterization of polymer electrolyte systems based on blends of poly(ethylene oxide) and poly(trimethylene carbonate) host matrices, with lithium as guest salts, are described in this study. Electrolytes with lithium salt compositions of n between 5 and 15 (where n represents the total number of cation coordinating units per lithium ion) and a component of (O=COCH2CH2CH2O) units between 5 and 15 wt%, were prepared by co-dissolution in acetonitrile. The solvent casting technique was used to produce flexible, transparent and free-standing films of electrolytes which were characterized by measurements of conductivity, cyclic voltammetry, differential scanning calorimetry and thermogravimetry.

**References**

[1] D. E. Fenton, J. M. Parker, P. V. Wright, Polymer 14 (1973) 589.
[2] M. B. Armand, in Polymer Electrolyte Reviews – 1 (Edited by J. R. MacCallum and C. A. Vincent), p. 1. Elsevier, London (1987).
[3] M.B. Armand, J.M. Chabagno, M.J. Duclot, Proceedings of the Second International Conference on Solid Electrolytes, St. Andrews, Scotland, 1978.

# Sol-Gel Derived Poly(ε-Caprolactone)/Siloxane Biohybrids With Application In Electrochemistry

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Owing to their technological impact in the domain of solid state electrochemistry, polymer electrolytes [1] have attracted significant interest in the last two decades, in particular for the fabrication of advanced batteries, sensors and electrochromic and photoelectrochemical devices [2]. Numerous $Li^+$-doped ormolyte systems obtained through the sol-gel method [3] have been investigated in the last few years [4].In the present work we have used Fourier Transform infrared (FT-IR) and Raman (FT-Raman) spectroscopies to study the extent of ionic association in a family of sol-gel derived lithium triflate ($LiCF_3SO_3$)-doped di-urethane cross-linked poly(ε-caprolactone)(PCL)/siloxane hybrid electrolytes introduced recently [5]. The PCL/siloxane host hybrid matrix is attractive, as it is expected to have lower environmental impact than that those currently used in commercial devices. Because of its biocompatibility, biodegradability and permeability, PCL has been widely used as biodegradable suture, artificial skin, resorbable prosthesis and container for drug delivery. The amorphous hybrid materials examined combine acceptable levels of ionic conductivity ($4.0\times10^{-6}$, $1.0\times10^{-6}$ and $6.7\times10^{-5}$ S $cm^{-1}$ at 35, 50 and 104 °C, respectively [5]) with biodegradability. In this work we have been specifically concerned with the description of the local chemical environment around the $Li^+$ ions and the triflate ions in the PCL/siloxane framework with the primary objective of gaining insight into the ionic conductivity mechanism.

**References**

[1] Armand M, Duclot MT, Chabagno JM (1978) In: Proceedings of the Second International Meeting on Solid State Electrolytes, St. Andrews, Scotland, Extended Abstract 6.5.
[2] Gray FM (1997) Polymer Electrolytes, RSC Materials Monographs. The Royal Society of Chemistry, London.
[3] Brinker CJ, Scherer GW (1990) Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing. Academic Press, San Diego CA
[4] (a) Judeinstein P, Titman J, Stamm M, Schmidt H, (1994) Chem Mater 6:127; (b) Dahmouche K, Atik M. Mello NC, Bonagamba TJ, Panepucci H, Aegerter MA, Judeinstein P (1997) J Sol-Gel Sci Technol 8:711; (c) de Zea Bermudez V, Alcácer L, Acosta JL, Morales E (1999) Solid State Ionics 116:197
[5] Nunes SC, de Zea Bermudez V, Silva MM, Smith MJ, Morales E, Carlos LD, Sá Ferreira RA, Rocha J, Journal of Solid State Electrochemistry, 10(4) (2006) 278.

# Sputtered PtIr thin films for bioengineering and electrocatalytic application

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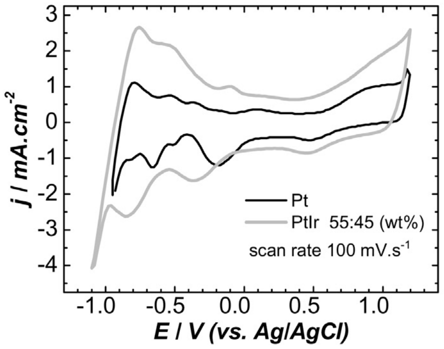
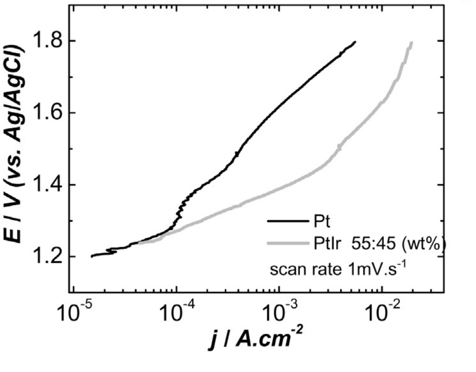
The research reports on the physical and electrochemical properties of PtIr thin films prepared by magnetron dc co-sputtering from Pt and Ir targets in argon plasma. The influence of the sputtering parameters such as argon partial pressure, dc power of each of the metal targets and the distance of the substrate from the targets on the film composition, surface structure and morphology was studied by variety of methods for bulk and surface analysis: XRD, SEM, EDX, XPS, and SIMS. The electrochemical behaviour of the films was investigated in neutral and acid aqueous solutions (0.9% NaCl and 0.5M $H_2SO_4$) at room temperature, using the electrochemical techniques of cyclovoltammetry, steady state polarisation, and electrochemical impedance spectroscopy. It was found that by optimisation of the sputtering process it is possible to obtain PtIr layers with improved mechanical and electrochemical characteristics relative to the monometallic Pt and Ir films sputtered at the same conditions. The composition, microporosity, density, specific surface area, etc. can be changed in order to influence the electronic conductivity, charge delivery capacity, impedance, catalytic activity, etc. The sputtered bimetallic films have shown high charge delivery capacity in physiological solution combined with low impedance in the frequency range of 1 to 10 Hz, typical for the biostimulation. They can be successfully used as top layers for signal recording and stimulating electrodes in the field of functional electrostimulation. In addition, it has been found that by varying the Pt:Ir ratio the catalytic activity towards hydrogen and/or oxygen evolution reactions can be enhanced or even bifunctional catalytic properties (e.g. acceleration of both the oxygen evolution and oxygen reduction reactions) can be achieved. Therefore, these films are also suitable for application as electrocatalysts in the electrochemical energy converters - hydrogen/oxygen fuel cells, water electrolysers, and unitized regenerative fuel cells.

**Ciclovoltametric curves in physiological solution**



**Polarisation curves of $O_2$ evolution in 0.5 M $H_2SO_4$**



# An aptamer-based QCM biosensor

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IgE levels are often raised in allergic diseases and grossly elevated in parasitic infestations. Therefore, a raised level of IgE aids, the diagnosis of allergic diseases, e.g. asthma, eczema and hay fever. Typical IgE levels of sensitised patients in serum correspond to 0.3 μg/ml.

We developed a quartz crystal biosensor using model system with human IgE as the analyte and DNA aptamer as immobilized receptor. The poly(amidoamine) (PAMAM) dendrimers of fourth generation (G4) and 1-hexadecanethiol (HDT) has been used for formation of self assembled monolayers on a gold surface for preparation of aptamer-based QCM biosensor. We combined the special properties of dendrimers with the SAMs concept to prepare the highly sensitive sensing surface on a gold-coated chip. Dendrimer terminated with the amino groups was used to anchor receptor, while the thiol chains serve as the stabilizing components. The advantage of this architecture in comparison to SAMs is higher local concentration of the terminal groups near the sensor surface, which can be functionalized. The biotynilated DNA aptamer was anchored on a surface of G4-HDT layers covered by neutravidin molecules. Neutravidin was crosslinked with PAMAM dendrimers via glutaraldehyde. The most important step in the immobilization procedure was reducing the Shiff base. The detection limit was of 100 ng/ml IgE. In addition, the aptamer receptors tolerated repeated layer regeneration after analyte binding and recycling of the biosensor with little loss of sensitivity.

In conclusion, we could show the suitability of DNA aptamer receptor on biosensor for sensitive and specific IgE detection. The determination of IgE alone will not predict an allergic state, since genetic and environmental factors also play an important role in the expressions of clinical symptoms.

Acknowledgements

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# Nanostructured electrode materials obtained from fluorine containing electrolytes of manganese with additives of copper(II) or lithium ions

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As shown in [1] the prospective method of making active electrode materials in power sources is the direct regulation of defects concentration in them. In this work we studied the influence of electrochemical dopation of manganese dioxide by copper and lithium ions upon its electrochemical and physicochemical properties. The products of anode oxidation of manganese(II) ions at the presence of additives of copper and lithium ions (see below) were synthesised electrochemically from fluorine containing electrolytes [2]. It is known that manganese dioxide form family of tunnelled polymorphs capable of intergrowth of their tunnels [3]. The polyphase composition and the grain size was analysed by the program Powder Cell v. 2.4. The evaluation of the latter showed anomalous dispersity of the samples (2—10 nm). The typical multiphase sample doped by $Cu^{2+}$ (0.02 $m{\cdot}L^{-1}$) showed the presence of 85% of $\gamma$- 15% of $\alpha$- and 5% of $\varepsilon$- polymorphs of manganese dioxide respectively. Addition of copper (lithium) ions causes the shift of XRD pattern peaks and increases the structure ordering. Lithium as a dopant stabilises $\alpha$-polymorph of manganese dioxide. Growth of the lithium content causes the expanding of the unit cell (Fig. 1) and correlates with electrochemical activity. In turn the content of copper in samples correlates with the ratio $Mn^{3+}/Mn^{4+}$ (Fig. 1) and also makes an impact on the electrochemical activity at galvanostatic discharge of these materials in 9M KOH (Fig. 2).

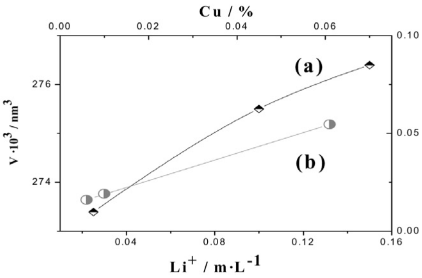

**Fig. 1.** The correlation of the lithium content in electrolyte with the unit cell volume (a) and copper content in the doped samples with the $Mn^{3+}/Mn^{4+}$ ratio (b).

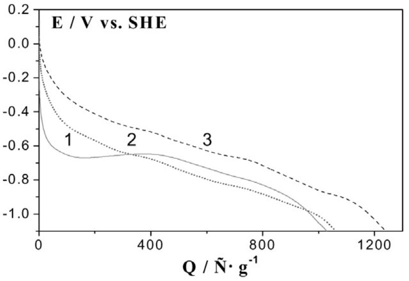

**Fig. 2.** The discharge curves of the undoped sample 1 and doped by copper samples: 2 (0.001M of $Cu^{2+}$ dopant in electrolyte); 3 (0.002M $Cu^{2+}$) in 9M KOH at a constant current density of 6 $mA{\cdot}cm^{-2}$.

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1 M. Kakazey, N. Ivanova, S.Ivanov, Y.Boldurev, G. Sokolsky et al. Journal of Power Sources 114 (2003) p. 170.
2 G. Sokolsky, S.Ivanov, N. Ivanova, Y.Boldurev. Powder Metallurgy and Metal Ceramics 45 (2006) p. 158.
3 S. Turner, P.R. Buseck. Nature 304 (1983) p. 143.

# Rose Bengal Monolayer based on High Quality Bilayer for Molecular Device

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Molecular electronics has the potential to enable a future generation of smaller and more densely integrated electronic devices. It has been reported that some organic molecules with appropriate electronic properties can be used for rectification, amplification, negative differential resistance and conductance switching.[1] Hence, the assembly and the ordering of the molecules on solid surface are important. The fabrication of self-assembled monolayer (SAMs) of organic molecules, formed spontaneously on solid substrates by adsorption from solution, has been intensively studied as a powerful method of surface modification and functionalization.[2] SAMs allow the control of chemical (or physical) interfacial processes and can offer distinct advantages in uniformity of structure and potentially lowered fabrication costs.

In the molecular electronics, it is important to have a high quality organic monolayer for the formation of defect free films and the surface roughness offset by molecular length which may find applications in molecular device. Since typical organic molecules for SAMs are 1~2 nm long, the surface roughness of solid substrate is an important factor. And also, electrical short problems in SAMs happen upon vapour deposition of the top electrode. So, there are many attempts to prevent electrical short in SAM. We proposed preparing the rose bengal (RB) monolayer on the thiol-terminated bilayer (TUA-AUT) with simple alkanethiol by a stepwise method to reduce the electrical short.[3] The 11-amino-undecane-1-thiol (AUT), a height is about 1.8 nm, is a bi-functional building block (about 3 to 4 nm) and it can form the thiol-terminated bilayer structure by hydrogen bonding between the amine group of an aminoalkanethiol monolayer on a gold surface and the free amine group of aminoalkanethiolates in a bulk solution without further treatments. In this presentation, we will report characterization of thiol terminated SAMs using surface sensitive techniques and application of the metal|SAM|metal molecular junction.

1. M. A. Reed, and T. Lee Molecular Nanoelectronics 2003, American Sci., J. M. Tour Molecular electronics 2003, World Sci., Y. Yang, J. Ouyang, L. Ma, R. J. Tseng, and C.-W. Chu J. Fun. Mat. 2006, 16, 1101.
2. J. Christopher Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, and G. M. Whitesides *Chem. Rev*. 2005, 105, 1103.
3. G. S. Bang, J. Park, J. Lee, N.-J. Choi, H. Y. Baek, and H. Lee *Langmuir* 2006 in press.

# (Opto)electrochemistry of PbS NC’s deposited onto ITO substrates

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Semiconductor nanocrystals (NC) have proven to be an active area of interest but, to date, the investigations have concentrated mainly on their optical properties. However for electronic devices or other applications where the charge carriers are to be extracted and utilized, e.g. solar cells, it is of utmost importance to know the electrochemistry and the (opto)electrochemistry of the semiconductor particles. In this respect materials such as PbS have the added advantage that they are active in the near infrared region of the spectrum and so have the possibility to access parts of the spectrum not presently addressable by any commercially available dyes.

The focus of this investigation primarily deals with the electrochemical and (opto)electrochemical properties of lead sulfide (PbS). For the experiments ITO (Indium-Tin-Oxide) electrodes were successfully derivatised with a sub-monolayer of MPTMS (3-mercaptopropyltrimethoxysilane) and subsequently modified with the PbS NCs. Amongst the electrochemical techniques employed for their characterization were cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Investigations were performed on all three interfaces, (bare ITO, ITO derivatised with MPTMS and the PbS modified ITO) and, as the PbS NCs are expected to be photoactive, all experiments were carried out both under conditions of illumination and non-illumination in order to eliminate effects due to ambient light.

Measurements of the photocurrent as a function of the applied potential were undertaken in order to determine the energetic position of the conduction band and, as the band-gap of the NC’s employed in these experiments is known from the optical characterization, the position of the valence band can be determined.

Further to this it is intended to investigate the charge carrier transfer rates of the PbS-NCs, which can be determined using IMPS (intensity modulated photocurrent spectroscopy) and consequently gain insights pertaining to the device efficiencies, i.e. how many electrons per photon can be extracted in such a system.

# Detection of low-molecular-weight pesticides by an acetylcholinesterase-based SPR biosensor

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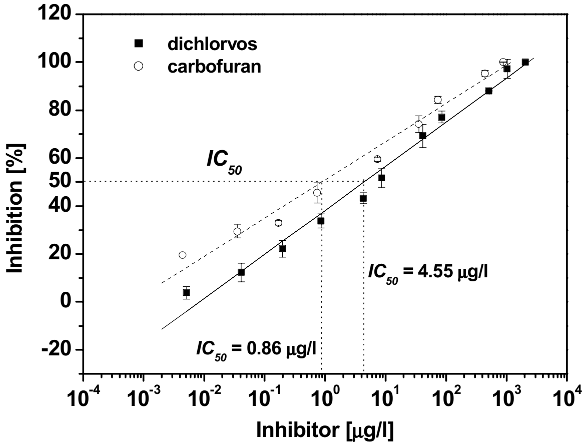
Organophosphate and carbamate pesticides can have the adverse effects on the environment and also enter food chain causing the harmful health effects in humans. Acute organophosphates and carbamates toxicity is primarily caused by the inhibition of the enzyme acetylcholinesterase. This study presents a multichannel enzyme-based biosensor on surface plasmon resonance (SPR) for detection of low-molecular-weight pesticides, carbofuran and dichlorvos, using a direct assay. The enzyme layers were formed on the dendrimer-modified gold sensor surface. Poly(amidoamine) (PAMAM) dendrimers have been used to improve the operational characteristics of enzyme-based biosensor. This improvement results from increased surface area that facilitates the immobilization of more enzyme molecules and increased total number of enzyme active sites. Using the SPR biosensor, it was possible to detect carbofuran and dichlorvos with respective detection limits of 0.001 and 0.014 μg/l.



These results indicate that the propose assay could serve as a prescreening tool, e.g. in food analysis laboratory. The sensitivities of pesticide detection were higher compared to those obtained by QCM. The detection limits reach the level actually accepted by the EU.

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# ITO nanoparticles – silicate – polyallylamine film modified electrode for ABTS$^{2-}$ - Laccase system immobilisation

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The recent development of biomolecule modified electrodes have attracted a lot of interest. This is connected with their potential applications for electrochemical devices as bioelectrochemical sensors [1], biofuel cells [2] and other bioelectronic applications [3]. The suitable framework plays crucial role for the construction of biomodified electrode.

The stable immobilisation of laccase together with mediator 2,2'-azino-bis-(3-ethylbenzothiazoline) sulfonate (ABTS) is challenging because of potential application of this system for dioxygen reduction [4]. Here, we applied for this purpose thin film composed of three elements. Each of them have their specific function: (i) tin-doped indium oxide nanoparticles (ITO) extend active electrode surface [5], (ii) polyallylamine (PAA) polymer capable to attract ABTS and prevents its escape into the aqueous solution [6] and (iii) hydrophilic silicate provides is a good framework for laccase encapsulation [4].

The electrode preparation employs deposition of the ITO nanoparticles (21 nm diameter) by subsequent immersion and withdrawal from their suspension. Next, ABTS is deposited at the electrode surface from the aqueous solution. This is followed by the deposition of PAA and sol-gel hydrophilic tetramethoxysilane based sol containing laccase from *Cerrena unicolor*.

These electrodes show catalytic activity towards dioxygen reduction. The presence of the ITO nanoparticles at the electrode surface considerably increases density of the catalytic current. The efficiency of the electrode process is larger that that obtained with carbon - silicate composite electrodes modified with ABTS - laccase system [7].

1. A.K. Wanekaya, W. Chen, N.V. Myung, A. Muchandani, Electroanalysis 18 (2006) 533.
2. A. Heller, Phys. Chem. Chem. Phys. 6 (2004) 209.
3. E. Katz, I. Willner, Chem. Phys. Chem 5 (2004) 1084.
4. D. Quan, Y. Kim, W. Shin, J. Electroanal. Chem. 561 (2004) 181.
5. J.H. Thomas, J.M. Drake, J.R. Paddock, S. Conklin, J. Johnson, C.J. Seliskar, H.B. Halsall, W.R. Heineman, Electroanalysis 16 (2004) 547.
6. J. Niedziolka, K. Szot, F. Marken, M. Opallo, Electroanalysis in press.
7. W. Nogala, E. Rozniecka, J. Rogalski, M. Opallo, Electrochem. Commun. 9 (2006) 1850.

# Sum-Frequency Generation spectroscopy at the electrochemical interface of a synthesized stellar dust cyanoethylene molecule adsorbed on Au(111)

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Cyanoethylene molecules were discovered in stellar dusts and nebulars and their properties have begun to be investigated and synthesized from this period. In this communication, we present and discuss the results of the investigation of the adsorption processes of cyanoethylene on a gold single crystal electrode, using *in situ* Visible-Infrared Sum-Frequency Generation (SFG) spectroscopy and cyclic voltammetry. The aim of the present work -which is in the preliminary stage- is to study the effect of the static electrical interfacial field on the adsorption geometry of HCCCN molecule. Indeed, SFG is a unique tool to have access to the orientation of the adsorbed molecule and hence to gain information on its interactions with the substrate. SFG is thus especially suitable to the unambigous identification of the bound adsorbate moiety and its evolution with the applied potential on the gold electrode.

# Oxygen reduction on nanostructured gold electrodes

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The electrochemical reduction of oxygen on gold electrodes has been widely studied. The reaction is highly structure-sensitive in both acid and alkaline media, Au(100) being the most active plane that catalyses the 4e$^-$ reduction of $O_2$ in alkaline solution at low overpotentials [1]. Gold nanoparticles (AuNP) have shown a remarkable catalytic activity for $O_2$ reduction and there has been a growing interest in determining the effect of particle size on this reaction [2]. AuNPs are used for various electronic applications.

In the work reported here, the reduction of oxygen was studied on thin-film gold electrodes in 0.5 M $H_2SO_4$ and 0.1 M KOH using the rotating disk electrode technique, aiming at establishing the effect of film thickness on the kinetics of $O_2$ reduction. Thin films of gold, with the nominal thickness of 0.25 to 20 nm, were prepared by vacuum evaporation onto a GC substrate and were coated with a Nafion® film. The earlier AFM studies have shown that separate gold clusters are evident at lower Au loading, whereas for the 5 nm and thicker films the substrate surface is completely covered with gold [3].

Current-potential curves for $O_2$ reduction on thin-film Au electrodes in 0.5 M $H_2SO_4$ showed a single reduction wave and were similar to those of bulk Au. The half-wave potential of $O_2$ reduction shifted to negative direction as the thickness of the Au film decreased. The specific $O_2$ reduction activity of the gold film electrodes was slightly lower than that of the bulk Au and was not significantly dependent on the loading of gold. The RDE data analysis revealed that the number of electrons transferred per $O_2$ molecule ($n$) was *ca*. 2 at the potentials $E > -0.2$ V *vs.* SCE, but it increased at the more negative potentials, indicating the further reduction of $H_2O_2$. The latter process was dependent on the film thickness, being less significant for the thinner films. The Tafel plots were linear between 0 and 0.2 V, showing slope values close to -120 mV/dec.

In alkaline solution, two-wave *I-E* curves typical for polycrystalline gold electrodes were registered for thin-film Au electrodes. For the electrodes of higher Au loading the current maxima were observed at ca -0.4 V *vs*. SCE. The value of $n$ of about 3.5 was found for these electrodes at the potentials of pre-wave indicating that the main product of $O_2$ reduction is $OH^-$. For the thinner films, the further reduction of peroxide was not observed at low overpotentials and the values of $n$ were close to 2 at $E > -0.6$ V vs SCE. This is an indication that the fraction of the Au(100) domains on the surface has to be smaller for separate Au clusters observed at low Au loadings than for the thicker films. The specific $O_2$ reduction activity increased with increasing the film thickness and this is the expected behaviour when the fraction of the most active (100) domain increases.

**References**

[1] R. Adži , in: J. Lipkowski, P.N. Ross (Eds.), Electrocatalysis, Wiley-VCH, New York, 1998, p. 197.
[2] S. Guerin, B.E. Hayden, D. Pletcher, M.E. Rendall, J.-P. Suchsland, J. Comb. Chem. 8 (2006) 679.
[3] A. Sarapuu, K. Tammeveski, T.T. Tenno, V. Sammelselg, K. Kontturi, D.J. Schiffrin, Electrochem. Commun. 3 (2001) 446.

# A Novel Photosensitization System: Electron Donor and Photosensitizer Incorporated into $TiO_2$ Gel Matrix

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$TiO_2$ is the most interesting photoelectrode in photosensitization system mainly because of its chemical stablility [1]. Generally photosensitization is fulfilled on the surface of $TiO_2$ electrode by chemical absorption of dye, and electron donor or acceptor is added in electrolyte solution [1-3]. In this report, a novel photosensitization was performed by incorparation of dye protoporphyrin IX (PPIX) and/or electron donor ferrocenecarboxylic acid (FcCOOH) into $TiO_2$ precursor Ti-$(OBu)_4$ via chemical bonds before $TiO_2$ gel formation. Then ultrathin photoelectrode composed of PPIX and/or FcCOOH in $TiO_2$ matrix was prepared on ITO glass by doctor-blade technique. Transient photocurrent measurement at wavelength of 442 nm shows a reduction photocurrent for the photoelectrode of PPIX-$TiO_2$ matrix in aqueous solution saturated with $O_2$ at the applied potential of 0.0 V vs. Ag/AgCl (Fig. 1). While $TiO_2$ matrix in the absence of PPIX shows little photocurrent becuase $TiO_2$ gel has little absorption at 442 nm (Fig. 1). This indicates PPIX can sucessfully sensitize $TiO_2$ matrix. When FcCOOH is incorparated into $TiO_2$ matrix with PPIX, the photocurrent is observed an order of magnitude larger than that of PPIX-$TiO_2$ matrix (Fig. 1). We also measured the photocurrent of FcCOOH incoporated in $TiO_2$ matrix (Fig. 1) and found that the value is decreased by more than 6 times compared to that of both FcCOOH and PPIX present in the matrix. This elucidates that FcCOOH acts not only as electron donor and charge carrier in $TiO_2$ matrix, but also as photosensitizer.

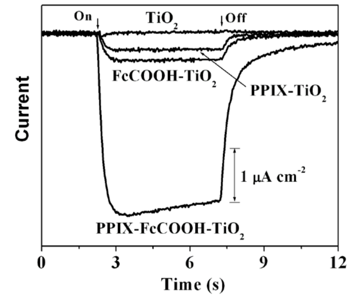

Fig. 1 Photocurrent transients of photoelectrodes in 0.1 M LiCl aqueous solution at 0 V vs. Ag/AgCl.

## References

[1] B. O'Regan, M. Graetzel, Nature 3531 (1991) 737.
[2] I. Robel, V. Subramanian, M. Kuno, P. V. Kamat, J. Am. Chem. Soc. 128 (2006) 2385.
[3] K. E. Splan, A. M. Massari, J. T. Hupp, J. Phys. Chem. B. 108 (2004) 4111.

# A Mediator-Type Nanocomposite Biosensor Based on Bacterial Cells

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The integration of biological molecules and novel nanomaterial components is of great importance in the process of developing new nanoscale devices for future biological, medical, and electronic applications. Since their re-discovery in 1991, carbon nanotubes (CNT) have attracted considerable interest due to their significant properties like high surface area, ability to accumulate analyte, minimization of surface fouling and electrocatalytic activity. Because of their high electrical conductivity CNTs are used as electrode material where they can facilitate electron-transfer between the electroactive species and electrode, and provide a new avenue for fabricating chemical sensors or biosensors (1).

Microbial biosensors are devices incorporating a microbial system that can specifically recognize species of interest, either intimately connected to or integrated within a proper transducing system. The transducer is the responsible for the quantitative conversion of the biochemical signal into an electronic signal that can be suitably processed and outputted. In this way, analytes of interest may be measured by using the assimilation capacity of the microorganism as an index of the respiration activity or of the metabolic activity. The major application of microbial biosensors is in the environmental field. Real-time analysis, simplicity of operation, portability, sensitivity and specificity of the microbial biosensor make these tools very attractive.

In this study, the effect of CNT on a mediator type microbial sensor response in terms of electron transportation was searched. For this aim, *Pseudomonas fluorescens* was used as a biological material and a composite chitosan membrane including bacterial cells and CNT was prepared and then cross-linked with glutaraldehyde. The characterization and optimization of the system were performed by using glucose as a substrate. Amperometric measurements were performed in the presence of different redox mediators such as potassium hexacyanoferrate (III), [HCF(III)] and ferrocene by means of a potentiostat. In order to investigate the contribution of CNT on the biosensor response, obtained results under the optimum conditions were compared with that of the composite bacterial sensor without CNT.

## REFERENCES

1. B.perez et. al. Journal of Nanoscience and Nanotechnology,5,(2005) 1694p

# Influence of Organic Solvents on the Inhibition by Paraoxon of the Immobilized Acetylcholinesterase

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The use of pesticides (insecticides, herbicides, fungicides) in agriculture has progressively increased after World War II, when increasingly large quantities of artificial chemical compounds were introduced to fight pest [1-4].

These toxic substances have a harmful effect against the insects and the mammals, but also present an important danger on human being, since they act on the level of the nervous system. The toxicity of organophosphorous pesticides is attributed to their ability to inhibit acetylcholinesterase (AChE), which catalyses the hydrolysis of the neurotransmitting agent acetylcholine (ACh).

A simple, reproducible and stable AChE amperometric bioelectrode [2, 4] was used following two experimental protocols, for measuring the enzyme activity before and after the incubation with paraoxon dissolved in polar and non-polar solvent.

The aim of this paper was to demonstrate the influence of polar (acetonitrile) and non-polar (n-hexan, n-heptan) organic solvents on the activity of the immobilized AChE on a bioelectrode, as well as the synergetic influence of these solvents on the inhibition process induced by paraoxon. In the same time, a kinetic treatment of the amperometric bioelectrode response allowed evidencing the influence of the organic solvents on the mechanism of AChE inhibition by paraoxon.

The inhibition percentage observed for paraoxon non-polar solutions increased in the following sequence: acetonitrile < water < hexan, suggesting that the paraoxon repartition between the non-aqueous solvent and the essential water for enzyme activity plays an important role in establishing the detection limit of the bioelectrode. Considering the AChE denaturation, induced only by the organic solvent, as a pseudo-inhibition process, the kinetic treatment of the bioelectrode response revealed that it follows a mixed competitive/non-competitive mechanism, while the inhibition due to a non-polar solution of paraoxon corresponds to a non-competitive/uncompetitive mechanism. In the last case, the cumulated inhibition effect was dominated by the inhibitor presence.

[1] Albareda-Sirvent M., Merkoçi A., Alegret S., Anal. Chim. Acta, **2001**, 442, *35-44*.
[2] Turdean G.L., “Acetylcholinesterase or Butyrylcholinesterase Amperometric biosensors for detection organophosphorus/carbamate pesticides in environmental area “ in “Recent trends in Acetylcholinesterase System” (Editors: Dr. Mahira Parveen and Prof. Santosh Kumar), IOS Press, Netherlands, **2005**, pp. *196-245*.
[3] Somerset V. S., Klink M. J., Sekota M. M. C., Baker P. G. L., Iwuoha E.I., Anal. Lettes, **2006**, 39, *1683-1698*.
[4] Turdean G.L., Popescu I.C., Oniciu L., Thevenot D. R., *J. Enzyme Inhib. Medic. Chem.*, **2002**, 17, *107-115*.

# Characterization of SIROF for neural electrostimulation – design and material considerations

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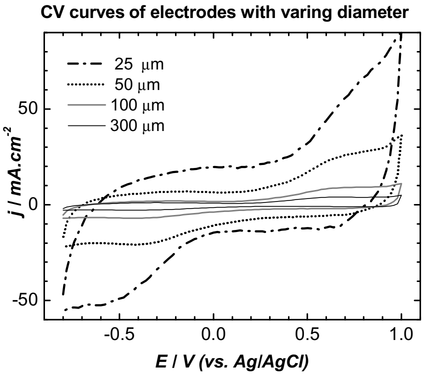
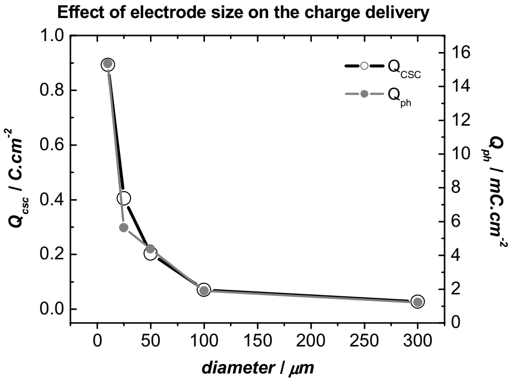
The paper presents experimental results obtained in the frame of a project on development of biohybrid electronic device for stimulation of single neural cells to artificially grow biological neuronal networks. The approach of combining electrical and biological signal processing in biohybrid circuits requires development of electroconductive, mechanically stable, and electrochemically active stimulating electrodes which must answer variety of strict requirements such as biocompatibility, high charge delivery capacity, low impedance, high corrosion resistance, stable long-term performance.. In addition, they must have a miniaturized geometry to match the limited space in the biological units and to ensure a good stimulation selectivity and enhanced spatial resolution. On the other hand, the smaller the electrode the lower the charge transfer and the higher the impedance of the phase boundary stimulating electrode/stimulated tissue. Thus, it is necessary on an electrode of limited size to integrate active surface as large as possible. This can be achieved by proper selection of the electrode material and modification of its surface structure and morphology. Other important factor is the nature of the sublayer material which determines the adhesion of the top layer and contributes to the total impedance of the stimulation system. In this study planar disk macro and microelectrodes of varying size with a functional top layer of reactively sputtered iridium oxide film (SIROF) upon different sublayers have been investigated using the electrochemical techniques of cyclovoltammetry, impedance spectroscopy and square potential waves. The charge delivery capacity and charge per phase values have been determined and discuss in regard to the electrode size and the type of the sublayer. The observed abrupt increase of the charge delivery capacity for the electrodes with diameters smaller than 100 μm has been prescribed to a transfer from linear to spherical diffusion of the charge carriers, affecting the kinetics of the charge transfer reactions. Some of the results are illustrated in the shown figures.





# Electrochromic electrodes modified by mixed nanoparticles of Ni/Co/Cd$(OH)_2$ nanoparticles.

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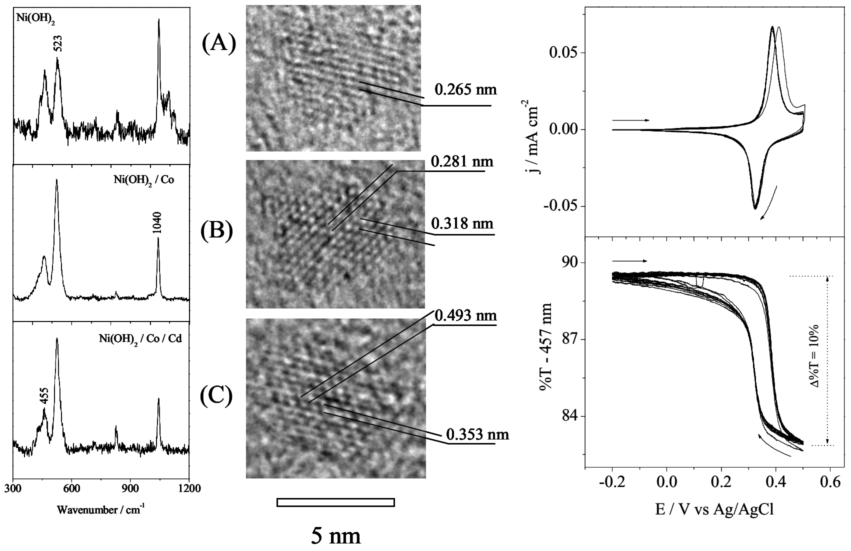
The present paper describes the characterization and electrochemical behavior of a new nanomaterial formed by a mixture of nickel, cadmium and cobalt hydroxides, synthesized by a sonochemical method. Particles of about 5 nm diameter were obtained and characterized by High Resolution Transmission Electron Microscopy and Raman spectroscopy. The nanoparticles were deposited onto ITO transparent electrodes by using the electrophoretic deposition technique providing electrochromic electrodes more homogeneous than those obtained by both electrodeposition and layer by layer technique.

Figure 1 shows the HRTEM micrographs and the Raman spectra of three nanoparticles, synthesized with different amounts of $Ni^{2+}$, $Co^{2+}$ and $Cd^{2+}$ in synthetic solution as follow: mol/mol (A) 100% $Ni^{2+}$, (B) 80% $Ni^{2+}$ / 20% $Co^{2+}$ and (C) 77% $Ni^{2+}$ / 20% $Co^{2+}$ / 3% $Cd^{2+}$. Nanoparticles of about 5 nm diameter with different crystallographic planes and interlamelar distances are seen when the amount of Ni atoms are changed. The Raman spectra shows that the presence of additives leads to a high number of structural defects and opened structures, denoted by the high intensity of the bands at 523 $cm^{-1}$ and 1040 $cm^{-1}$. Also, the electrochromic behavior of a Ni/Co/Cd hydroxide modified electrode prepared during by applying +1.0 V $cm^{-1}$ for 5 minutes is shown.. For this electrode an electrochromic efficiency of about 80 $C^{-1}$ $cm^2$ (457 nm) and switching times of 0.2 s were found.



# A Raney Nickel electrode revisited

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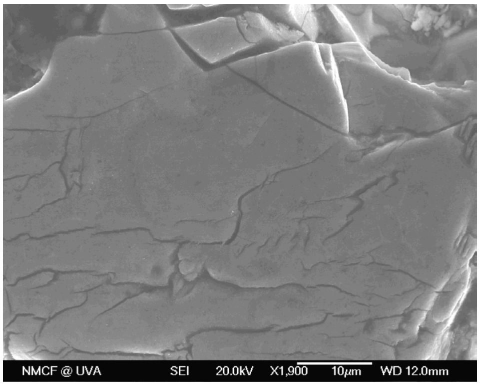
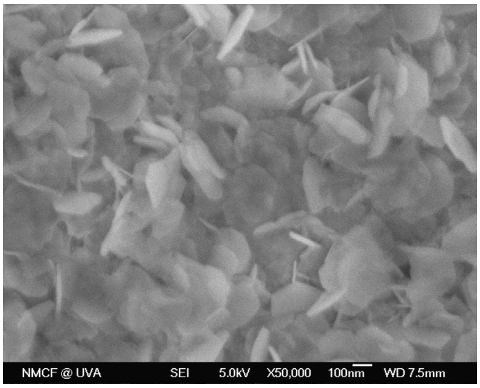
We explore the relationship between nanostructure and electrochemical properties of a commercial Raney Nickel – based air electrode (made by Gaskatel, De), used both as cathode or as anode in the alkaline fuel cells and electrolysers made by this company. The original microstructure of Raney-Ni results from leaching one component (Al, in our case) from the precursor Ni-based alloy. A hierarchy of pores are present, from micron-size crevasses (narrow and deep, see SEM image to the right) to holes few nanometers in size. An analysis of published data shows that Raney-Ni samples which are apparently similar from the chemical and morphological and points of view may have substantially different electrochemical properties. The causes of these discrepancies are poorly understood, but we suspect they may be partly due to slow reactions during cell operation (e.g. oxidation, formation of hydrides, loss of residual Al-Zn) which may be accompanied by extended “surface restructuring”. As a matter of fact, the picture at the right shows the modification of a grain of Raney Nichel (Ni-Al) after 24 hours of treatment in 30% KOH at 70°C, which brings the Al/Ni atomic ratio from 1/(7±2) to about 1/20.





We compare the polarization behaviour and impedance parameters (in 30w% KOH and room temperature) of the original Gaskatel electrode and of an air electrode after the above-mentioned treatment. This treatment is responsible for a substantial decrease of the performances in the hydrogen and oxygen evolution reactions (estimated exchange currents, overvoltages for 20 mA anodic or catodic currents); it also influences the behaviour of the electrode during oxidation and hydride formation. A comparison with the electrochemical response of a compact Ni-metal electrode suggests that these changes are mostly related to the change of morphology and the associated reduction of the electrode active area caused by treatment in hot KOH.

# High Activity of Electrocatalysts Deposited on CNT-based Electrode for Direct Methanol Fuel Cell

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Direct methanol fuel cell (DMFC) is an electrochemical device converting chemical energy into electric energy by feeding the methanol and oxidant (e.g. $O_2$ or air) to the anode and cathode, respectively. The redox reaction of DMFC provides theoretical potential of 1.21 V. However, the kinetic and activation overpotentials limit the reaction rate of the electrode, which reduces the cell voltage of 50% loss at practical current densities. Hence, the development of advanced electrode systems for redox reaction is a key issue of DMFC. The core component of DMFC, membrane-electrode-assembly (MEA), is a sandwiched structure including the anode, cathode and membrane. In the conventional process, the electrocatalyst (e.g. Pt or Pt-Ru) deposited on activated carbon mixed with Nafion® solution is screen-printed on gas diffusion layer (e.g. carbon cloth or carbon paper) as the electrodes. However, some electrocatalysts are isolated by the Nafion® solution, which leads to low utilization of electrocatalysts.

In this study, the fabrication of electrocatalysts deposited on carbon nanotubes (CNTs) directly grown on a carbon cloth as the electrode is applied in the DMFC. CNTs, which have high surface area and good electronic conductance, are suitable for electrocatalyst supports. The CNT was directly grown on the carbon cloth, and then electrocatalysts were subsequently deposited on the as-grown CNT. From electron microscopy images reveal that the graphene sheets of CNT not only adhere to the carbon cloth but also directly conjoined with the carbon cloth. The electrocatalysts with the size of 3 ~ 5 nm are uniformly dispersed on the CNT. The MEA using 0.4 mg $cm^{-2}$ Pt-Ru/CNT-CC, 3.0 mg $cm^{-2}$ Pt black and Nafion 117 as the anode, cathode and membrane, respectively, performs very well in a direct methanol fuel cell (DMFC) test. The cell performance shows that maximum power density is 102 mW $cm^{-2}$ at 80 °C. The micro-structural MEA analysis shows that the thin electrocatalyst layer is uniform, with good interfacial continuity between membrane and the gas diffusion layer.

# Micro- to Macro-Porous Silicon Formation by Means of Metal Particle Enhanced HF Etching

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Porous silicon (Si) has a wide range of pore sizes between nanometers and sub-millimeters [1]. Microporous Si that consists of nanometer-sized pores has attracted considerable attention due to its visible light emissions and net large surface areas. Macroporous Si that consists of micrometer-sized pores is expected to improve the conversion efficiency of solar cells [2-4]. Sensors including biosensors [1,5,6], light emitting devices, and silicon-on-insulator devices are expected as applications of porous Si [1]. Porous Si is usually prepared by electrochemical etching under anodic bias in a fluoride containing solution [1]. Recently, we have reported a preparation process of porous Si, via the modification of Si wafers with fine metal particles, followed by simple immersion in a HF solution, in which we dispense with a bias or a particular oxidizing agent [2-4]. This paper also describes the structure of porous silicon produced by metal particle enhanced etching.

Metal nanoparticles (Pt, Rh, Pd, Cu, Ag or Au) were deposited on n-Si wafers by electroless displacement deposition from a metal-salt solution containing HF. The metal-particle-deposited Si wafers were immersed in a simple aqueous HF solution. The etching rate and structure of porous Si varied according to the kind of metal on the Si wafer, photoillumination intensity or oxygen concentration in the HF solution. A continuous microporous Si layer, which gave photoluminescence in orange color, was formed on the Pt-particle-deposited n-Si wafer with low photoillumination intensity and oxygen concentration. Both micro- and macroporous Si layers were formed and the etching rate increased as the intensity and concentration increased. Ag nanoparticles, which were smaller than Pt particles, produced smaller macropores than those for Pt particle case. Absence of oxygen in the solution formed only macroporous layer on the Pt-particle-deposited n-Si. These results are explained by a local cell theory. The metal nanoparticles remained on porous Si were active as electrochemical catalyst.

[1] Lehmann, V. Electrochemistry of Silicon; Wiley-VCH: Weinheim, 2002.

[2] S. Yae, Y. Kawamoto, H. Tanaka, N. Fukumuro, H. Matsuda, Electrochem. Comm. 5 (2003) 632.

[3] S. Yae, H. Tanaka, T. Kobayashi, N. Fukumuro, H. Matsuda, Phys. Stat. Sol. (c) 2 (2005) 3476.

[4] S. Yae, T. Kobayashi, T. Kawagishi, N. Fukumuro, H. Matsuda, Solar Energy 80 (2006) 701.

[5] J.J. Kelly, X.H. Xia, C.M.A. Ashruf, P.J. French, IEEEE Sens. J. 1 (2001) 127.

[6] M.P. Schwartz, F. Cunin, R.W. Cheung, M.J. Sailor, Phys. Stat. Sol. (a) 202 (2005) 1380.

# The Electrochemical Impedance Spectroscopy of Poly (N-vinylcarbazole) onto Carbon fiber microelectrodes in different solutions and methods

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The electrochemical impedance spectroscopy of Poly(N-vinylcarbazole) P(NVCz) was electrodeposited on carbon fiber microelectrode (CFME), which is prepared by three different methods (Cyclic voltammetry, chronoamperometry, and chronopotentiometry) under different electrolytic conditions (Sodium perchlorate ($NaClO_4$), lithium perchlorate ($LiClO_4$) and tetraethyl ammonium tetrafluoroborate ($TEABF_4$) in the solvent of acetonitrile (ACN) (Figure 1a, b, and c). The effects of type of electrolytes, methods and film thickness were investigated in detail. Interaction and nano characterization of thin conjugated polymeric films on carbon surfaces, especially on micron sized carbon fibers, are recent interest (1-2) Due to needs modifications of their surfaces to understand the interfacial properties between fiber and matrix. The impedance responses were analyzed within a dual transmission line model. The Characterization of P(NVCz) was obtained by CV, Fourier transform infrared reflectance spectroscopy (FTIR- ATR) and Scanning electron microscopy (SEM). Electrochemical impedance spectroscopy (EIS) results of P(NVCz) which is prepared by chronoamperometric method in $LiClO_4$/ACN indicated that the modified CFME gave better capacitance behaviors i.e; specific capacitance ($c_{sp}=0.0713$ F $cm^{-2}$) and double layer capacitance ($c_{dl}=3.37x10^{-3}$ F $cm^{-2}$) than other methods (CV and Chronopotentiometric methods) and solutions type (0.1 M $NaClO_4$ in ACN and 0.1 M $TEABF_4$ in ACN) .However, the lowest solution resistance Rs=0.75 kohm, and polymerization resistance Rp=7.37 kohm of P(NVCz) was obtained by Chronoamperometric method in 0.1 M $LiClO_4$/ACN.

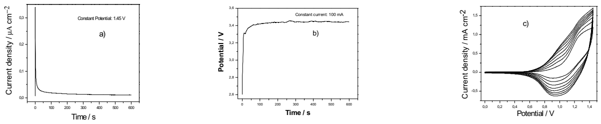

Figure 1. a) Polymer growth of NVCz deposited by chronoamperometric method (applied 1.45 V) b) by chronopotentiometric method (applied 100 mA) c) by CV method on CFMEs in 0.1 M $LiClO_4$ / PC. Scan rate: 100 mV $s^{-1}$, 8 cycles was taken between 0.0 and 1.4 V vs. Ag/AgCl, $[NVCz]_0=10^{-3}$.

[1] **A.S. Sarac**, Nanoscale Spectroscopic characterization of conductive polymer electrocoated carbon fiber surface, in H.S. Nalwa (Ed.), Polymeric Nanostructures, first ed., American Scientific Publishers, Valencia, CA, USA, 2006. (Chapter

[2] **A.S. Sarac**. in Herman, F. Mark (Ed.), Encrylopedia of polymer Science and Technology, vol.9 part 3, third ed., 2004.

# Fabrication of Ordered Nanoporous Garphitic $C_3N_4$ as an Efficient Catalyst Support for Direct Methanol Fuel cell

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Recently significant progress has been made in the synthesis of ordered nanoporous carbons by using mesoporous silica[1] and colloidal crystals[2] as solid templates. There have been also great interests on carbon materials containing heteroatoms such as N, B and Si due to the expectation of novel properties such as extreme hardness, oxidation resistance and chemical inertness. The most exciting materials among them are carbon nitride phases. Especially graphitic-$C_3N_4$ is a novel, rarely examined material which has extraordinary prospects in catalysis and hard coating and as adsorbents.[3,4] Despite of great interest in high surface area carbon nitride materials, it is difficult to produce extended nitrogen-rich carbon nitride with highly ordered nanoporous structure. The fabrication of well-ordered macroporous graphitic carbon nitride by condensation of cyanamide ($CN-NH_2$) as a molecular precursor using a colloidal silica crystalline array as a template is described in this work. The resulting sample exhibited a 3-dimensionally extended highly ordered pore array and revealed high graphitic nature with $C_3N_4$ stoichiometry. In particular, the $C_3N_4$ network structure consists of novel tri-s-triazine rings ($C_6N_7$) cross-linked by trigonal N atoms. In fuel cell, catalysts are usually supported on electronically conducting carbon with high surface area, which allow higher degree of dispersion of the catalysts. The performance and stability of the fuel cell are known to strongly depend on the carbon support used as well as the catalytically active metal species The nanostructured $C_3N_4$ when used as a support for Pt-Ru anode catalysts, resulted in much improved catalytic activity for methanol oxidation in DMFC probably due to its unique structural properties.

References:
[1] S. B. Yoon, J. Y. Kim, J.-S. Yu, *Chem. Commun.* 14 (2002) 1536.
[2] S. B. Yoon, G. S. Chai, S. K. Kang, J. -S. Yu, K. P. Gierszal,M. Jaroniec, *J. Am. Chem. Soc.*127 (2005) 4188.
[3] Q. Guo, Y. Xie, X. Wang, S. Zhang, T. S. Hou, *Chem. Comm.* 1 (2004) 26.
[4] M. Groenewolt, M. Antonietti, *Adv. Mater.* 17 (2005)1789.

# Functionalization of Single-Wall Carbon Nanotubes: a new promising nanomaterial for neurotransmitters detection

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Single-Wall Carbon Nanotubes (SWCNTs) have demonstrated a wealth of exceptional structural, mechanical, and electronic properties, which have made them potentially useful for applications in nanotube-reinforced materials, nanoelectronic devices, field emitters, and probe tips for SPM, and also for sensors, biosensors and actuators.

However, manipulation and processing of SWCNTs has been limited by their insolubility in most common solvents, although some dissolution has recently been obtained. Considerable effort has therefore been devoted to the chemical modification and derivation of carbon nanotubes, which might pave the way to many useful applications, including composite preparations, enzyme and biological molecules immobilization (for biosensor and electrochemical sensor applications). Attachment of oxygen functional groups (i.e., carboxylic, carbonyl, hydroxyl, quinone, lactone, phenol, etc.) on the carbon nanotubes surface could be achieved using different pretreatment of nanostructured materials. Considerable effort has therefore been devoted to the chemical modification and derivation of carbon nanotubes and success at covalent derivatization of purified SWCNT has been limited in scope. Different attempts at sidewall modifications have been hampered by the presence of significant graphitic or amorphous carbon contaminants or have required solubilization via chemistry on ends of cut . A more accommodating and direct approach to functionalized nanotubes is therefore required.

Particularly, the SWNT-modified electrodes were applied for the electrochemical determination of a series of neurotransmitters. The focus was on monamine neurotransmitters, given that these substances have many physiological roles, are critical for normal neuronal metabolism, and are involved in some neurological disorders such as Parkinson's disease. Thus real time measurements with practical and sensitive electrochemical tools could prove extremely useful for research into the etiology, therapy, and environmental modulators of disturbances related to neurotransmitters. We report here the sidewall functionalization of purified SWCNTs, obtained by different approaches and finally, we can discuss possible applications of functionalised SWCNT for detecting neurotransmitters such as dopamine, caffeic acid and epinephrine.

# Influence of surface specifications and chemical contents on electrochemical capacitor performance of manganese oxide

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It has already been shown that the nanostructure of the electrode affects charge–discharge properties of the pseudocapacitor, particularly at large current density [1]. Preparation of the electrode from nanostructured $MnO_2$ results in electrodes having large specific surface area and enlarges the contact area between active and conducting material [1, 2].

In this work, we report how the differences in surface specifications and chemical contents of various prepared manganese oxide samples by ultrasonic method [3] influence on capacitive behavior of $MnO_2$ in aqueous sulphate solution at different pH as electrolyte.

DC current charge and discharge cycling in electrolytes of different pH provide information on whether the protons or other cation dominate the surface reaction. The comparison of voltammetric charges at very high and very low sweep rate for various samples indicates the differences of the accessible surface sites of prepared manganese oxide [4]. The chemical content of $MnO_2$ determines using the potentiometric titration approach of Vetter and Jaeger [5]. Comparison between the results indicates that the electrochemical performance of the electrodes improves with increasing $Mn^{+3}/Mn^{+4}$ ratio and excess water as well as with enhancement of accessible surface site.

References

[1] S. Bach, J. P. Pereira-Ramos, N. Baffier, Solid State Ionics 80 (1995) 151.
[2] M. Hibono, H. Kawaoka, H. Zhou, I. Honma, J. Power Sources 124 (2003) 143.
[3] A. Zolfaghari, F. Ataherian, M. Ghaemi, A. Gholami, Electrochim. Acta (in press).
[4] S. Ardizzone, G. Fregonara, S. Trasatti, Electrochim. Acta 35 (1990) 263.
[5] K.J. Vetter, N. Jaeger, Electrochim. Acta 11 (1966) 401.

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