ELECNANO 4
7 ECHEMS

Fourth international edition of ElecNano
-
Seventh international edition of ECHEMS

23-26 May 2011, Paris, France

ElecNano^4- 7th ECHEMS
23-26 may 2011
Paris, France

Fourth international edition of Electrochemistry in Nanoscience

May 23-26, 2011, Paris, France.

Following the success of the previous editions of **ELECNANO 1-3** (2006, 2008 and 2009) and **ECHEMS 1-6**, the electrochemistry group of the French Chemical Society, the electrochemists of the University Denis Diderot Paris and the Scientific committee of the ECHEMS decided to join their effort to sort out a **joint meeting ElecNano^4 - 7th ECHEMS**. This edition is held in Paris from **May 23 to 26 of year 2011**.

The main topic of the meeting is:

Electrochemistry in Nano Structuration of Substrates and Energy

The major goals of the meeting are to show the contribution of electrochemistry in **nanostructuration of substrates** for energy with a special emphasizes into **molecular electrochemistry for photovoltaic, artificial photosynthesis and CO$_2$ reduction/valorisation**. The purpose of **ElecNano^4 - 7th ECHEMS** is to bring the leading scientists in electrochemistry and the scientists working in nanosciences and nanotechnology for energy to stimulate intensive discussion, initiate cooperation, and improve the personal links in these fields.

So Welcome in Paris and enjoy the meeting !!!

ElecNano^4- 7th ECHEMS
23-26 may 2011
Paris, France

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23-26 may 2011
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The organizing and scientific committee and the participants of the Elecnano^4 – 7th ECHEMS thank for their support the following organisms and companies.

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	Monday 23/5	**Tuesday 24/5**	**Wednesday 25/5**	**Thursday 26/5**
9 :00 - 9 :45		*Chairperson* : Hyacinthe RANDRIAMAHAZAKA **IL2 M. Gratzel**	*Chairperson* : Francesco PAOLUCCI **IL4 A. Deronzier**	*Chairperson* : Gunther WITTSTOCK **IL5 S. Palacin**
9 :50 – 10 :10		**OC 09 I. Rutkowska**	**OC 23 V. Jimenez**	**OC 33 A. Bonnefont**
10 :10 – 10 :30		**OC 10 N. Vlachopoulos**	**OC 24 J. Christophe**	**OC 34 D. Zigah**
10 :30 – 11 :00		**Coffee Break**	**Coffee Break**	**Coffee Break**
11 :00 - 11 :20		*Chairperson* : Bernd SPEISER **OC 11 S. Ahmad**	*Chairperson* : Steeve REISBERG **OC 25 S. Rapino**	
11 :20 – 11 :40		**OC 12 U. Tefashe**	**OC 26 P. Kulesza**	**Poster Session 2**
11 :40 – 12 :00		**OC 13 J. Elias**	**OC 27 W. Schuhmann**	
12 :00 – 12 :20		**OC 14 V. Guerin**	**OC 28 S. Cassaignon**	
12 :50-14 :00		**Lunch Break**	**Lunch Break**	**Lunch Break**
14 :00 – 14 :45	*Chairperson*: Alexander KUHN **IL1 G. Whitesides**	*Chairperson* : Jean Claude MOUTET **IL3 R. Zeissel**	*Chairperson* : Pascal MARTIN **OC 29 R. McCreery** **OC 30 M. Janin**	*Chairperson* : Jalal GHILANE **IL6 R. Crooks**
14 :50 – 15 :10	**OC 01 B. Fabre**	**OC 15 P. Laine**	**OC 31 E Maisonhaute**	**OC 35 G. Loget**
15 :10 – 15 :30	**OC 02 Y. Leroux**	**OC 16 J. Ludvik**	**OC 32 M. Hromadova**	**OC 36 J. Ustarroz**
15.30-15.50	**OC 03 F. Kanoufi**	**OC 17 Y. Zholudov**	**Coffee Break**	**OC 37 F. Mirkhalaf**
15 :50 – 16 :30	**Coffee Break**	**Coffee Break**	**Poster Session 1**	**Coffee Break**
16 :30 – 16 :50	*Chairperson* : Steen Uttrup PEDERSEN **OC 04 L. Santos**	*Chairperson* : Sophie GRIVEAU **OC 18 A. Taleb**		*Chairperson* : Cyrille COSTENTIN **OC 38 V. Artero**
16 :50 – 17 :10	**OC 05 M. Lillethorup**	**OC 19 P. Ugo**		**OC 39 C. Visy**
17 :10 – 17 :30	**OC 06 N. Plumeré**	**OC 20 L. Bouffier**		**OC 40 D. Merki**
17 :30 -17 :50	**OC 07 C. Perruchot**	**OC 21 A. Da Pozzo**		**END**
17 :50 - 18.10	**OC 08 M. Etienne**	**OC 22 V. Bonometti**		
20 :00		**Boat cruise**	**Banquet**	

ElecNano^4- 7th ECHEMS
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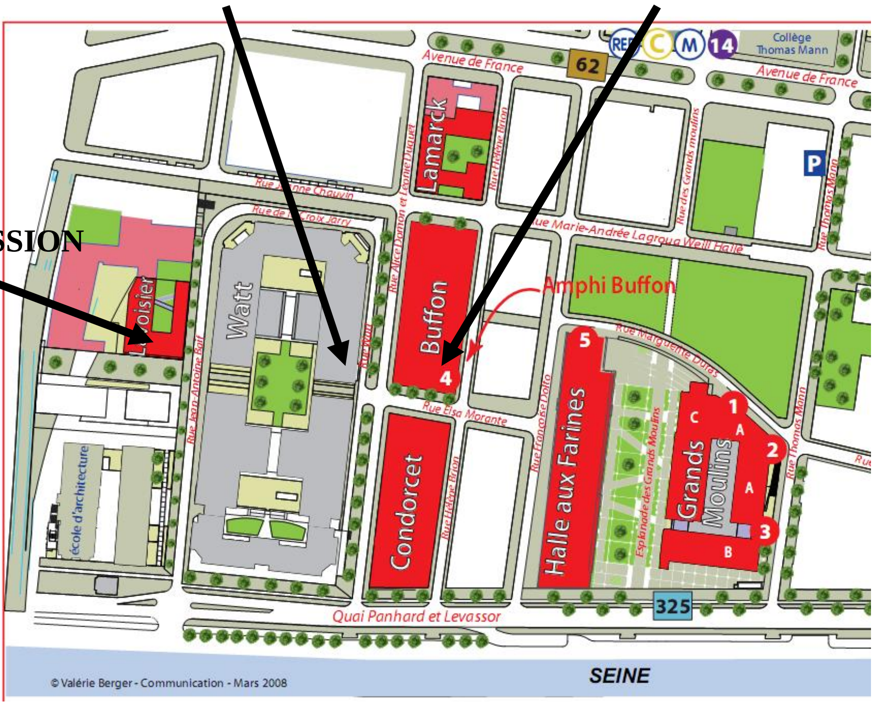
PLAN



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POSTER SESSION

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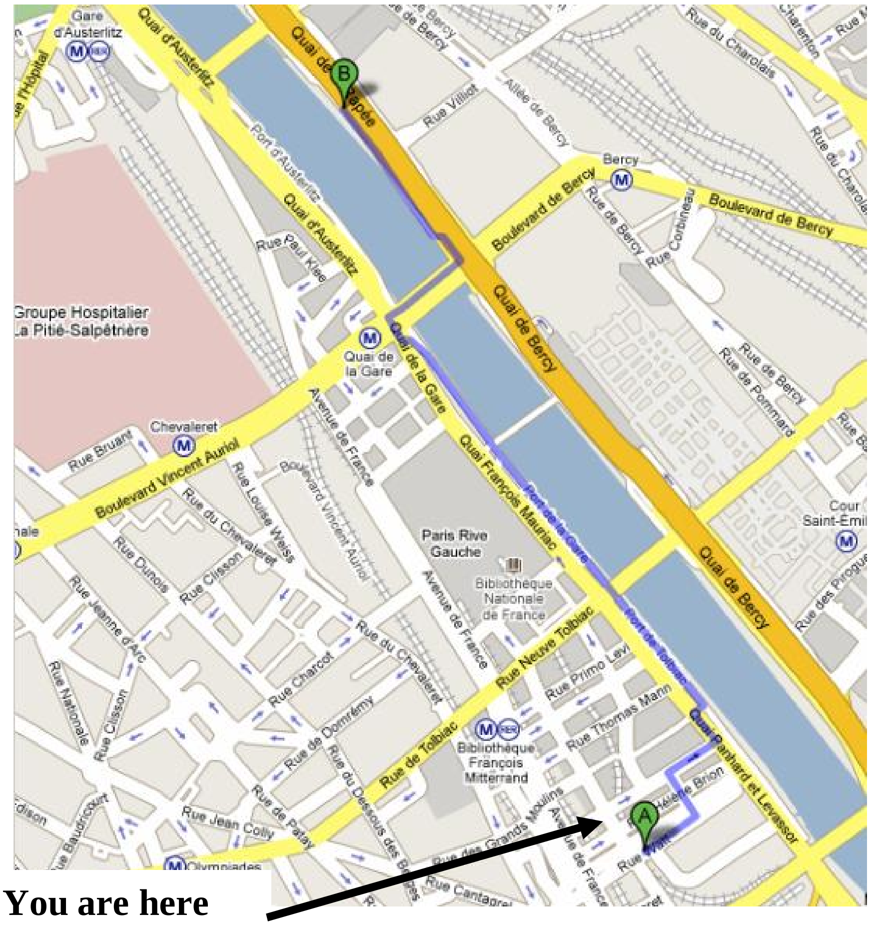

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MONDAY 23 MAY

14:00 - 14:45: IL1

G. Whitesides

14:50 - 15:10: OC 01

B. Fabre

Local Anodic Oxidation (LAO)-Directed Nanopatterning of Organic Monolayer-Modified Silicon Surfaces

15:10 – 15:30: OC 02

Y. Leroux

Use of Sylil Protecting Group in Diazonium Electrochemistry: Formation of Robust Binary Layer and Active Monolayer Covalently Bonded To Carbon Surfaces

15:30 – 15:50: OC 03

F. Kanoufi

Imaging the local electrochemical reactivity of surfaces by light reflectivity: application to the electrografting of aryldiazonium salts

15:50 – 16:30
Coffee break

16:30 – 16:50 : OC 04

L. Santos

Electroreduction of diazonium salts in aqueous medium via host –guest complexation and the formation of mix multifunctional organic materials

16:50 – 17:10 : OC 05

M. Lillethorup

Polymer Brushes and Their Application in Charge Transport Processes

17:10 – 17:30 : OC 06

N. Plumeré

Electrochemical Deprotection and Activation of Michael Acceptors for Electrode Microstructuration

17:30 – 17:50 : OC 07

C. Perruchot

Growth of polymer brushes initiated from
a surface functionalized by conducting polymer

17:50 – 18:10 : OC 08

M. Etienne

Electrochemically-assisted deposition of sol-gel materials: nano-structuration and modification of nano-objects

TITLE

G. Whitesides

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, USA

Abstract coming soon

Note IL1 :

LOCAL ANODIC OXIDATION (LAO)-DIRECTED NANOPATTERNING OF ORGANIC MONOLAYER-MODIFIED SILICON SURFACES

Bruno Fabre and Cyril Herrier

UMR 6226 CNRS/Université de Rennes, Sciences Chimiques de Rennes, Matière Condensée et Systèmes Electroactifs (MaCSE), Campus de Beaulieu, 35042 Rennes, France

The combination of monocrystalline silicon's well-defined structure and the ability to prepare hydrogen-terminated surfaces (Si-H) easily and reproducibly has made this material a very attractive substrate for immobilizing functional molecules. The functionalization of Si-H using the covalent attachment of organic monolayers has received intense attention due to the numerous potential applications of controlled and robust organic/Si interfaces (1). Unlike those of gold, silicon's electronic properties are tunable, and researchers can directly integrate silicon-based devices within electronic circuitry. Moreover, the technological processes used for the micro- and nanopatterning of silicon are numerous and mature enough for producing highly miniaturized functional electronic components. Among lithographic methods, scanning probe microscopy-related techniques have been demonstrated to be powerful for the fabrication of functional nanostructures on surfaces with high control on their composition and spatial resolution (2).

Herein, we describe our results on the local anodic oxidation (LAO) of densely packed organic monolayer-modified silicon surfaces with a conducting AFM tip. The generated silicon oxide nanopatterns are removed by dipping the surface in diluted HF. So, the resulting surface contains potentially reactive hydrogen terminated areas surrounded by an insulating organic matrix. The hydrogenated patterns are then used for the selective electroless deposition of gold particles (Figure 1). Such a deposition process is found to be highly dependent on the nature of the group end-capping the monolayer. Such metallized surfaces could be of interest in the development of nanoelectrode arrays with high control on their surface area and geometrical shape.

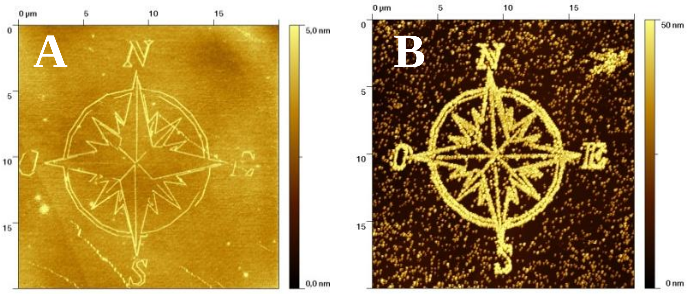


Figure 1. AFM images of silicon oxide patterns produced by LAO of hexadecyl-modified silicon surface before (A) and after etching in HF followed by immersion in a mixture of gold salt, HAuCl$_4$ and HF (B).

Reference:

(1) a) Fabre, B. *Acc. Chem. Res.* **2010**, *43*, 1509. b) Zigah, D.; Herrier, C.; Scheres, L.; Giesbers, M.; Fabre, B.; Hapiot, P.; Zuilhof, H. *Angew. Chem. Int. Ed.* **2010**, *49*, 3157.
(2) a) Wouters, D.; Schubert, U. S. *Angew. Chem. Int. Ed.* **2004**, *43*, 2480. b) Krämer, S.; Fuierer, R. R.; Gorman, C. B. *Chem. Rev.* **2003**, *103*, 4367.

Note OC-1 :

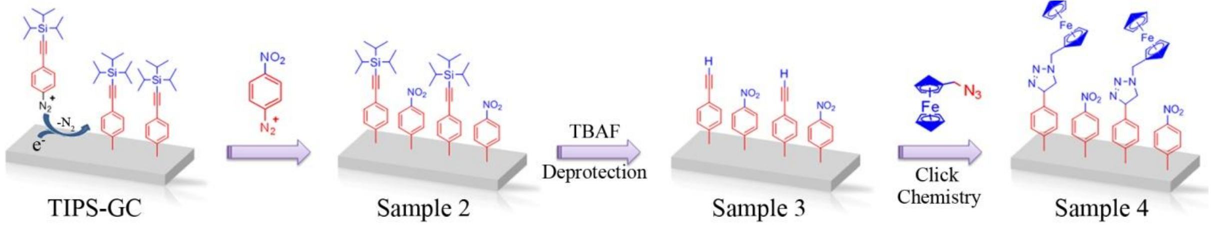
USE OF SYLIL PROTECTING GROUP IN DIAZONIUM ELECTROCHEMISTRY: FORMATION OF ROBUST BINARY LAYER AND ACTIVE MONOLAYER COVALENTLY BONDED TO CARBON SURFACES.

Yann R. Leroux,[a] Jean-Marc Noël,[a] Hui Fei,[a] Clément Roux,[b] Alison J. Downard,[b] and Philippe Hapiot[a]

[a] *Université de Rennes 1, Sciences Chimiques de Rennes (Equipe MaCSE), CNRS, UMR 6226, Campus de Beaulieu, Bat 10C, 35042 Rennes Cedex, France*
[b] *Department of Chemistry, University of Canterbury, MacDiarmid Institute Advanced Materials & Nanotechnology, Private Bag 4800, Christchurch 8140, New Zealand*

Recently, we have proposed a global strategy for preparing a versatile and robust reactive platform that could be used for immobilizing molecules on carbon substrates with controlled morphology and high selectivity.(1,2) The procedure is based on the electro-reduction of a selected triisopropylsilyl (TIPS)-protected ethynylaryldiazonium salt. It avoids the formation of multilayers and efficiently protects the functional group during the electro-grafting step. After TIPS deprotection, a dense reactive ethynyl aryl monolayer is obtained which presents a very low barrier to charge transfer between molecules in solution and the surface. As a test functionalization, azidomethylferrocene was coupled by "click" chemistry with the modified surface. Analysis of the redox activity highlights a surface concentration close to the maximum possible attachment considering the steric hindrance of a ferrocenyl group. Following electrochemical investigations strongly suggest that the reactive monolayer presents pinholes with a controlled assembly.

Tacking advantages of the properties of the molecular platform (**TIPS-GC**), we propose a development of this work to design binary films covalently bonded to carbon surfaces and with a controlled morphology. As an example for illustrating the methodology, we will report on a binary film consisting of electroactive ferrocene moieties attached via "click chemistry" to the acetylbenzene moieties and nitrobenzene groups that were electrochemically grafted into the pores of this new platform.



Scheme 2. Principle of the different modification steps using TIPS-GC electrode as starting material.

Reference:

(1) Leroux, Y.R. *et al. J. Am. Chem. Soc*. **2010**, *132*, 14039–14041.

(2) "Surface Patterning: More Than Just Scratching the Surface." *JACS Select #11*, Publication Date (Web): December 22, **2010**

Note OC-2 :

IMAGING THE LOCAL ELECTROCHEMICAL REACTIVITY OF SURFACES BY LIGHT REFLECTIVITY: APPLICATION TO THE ELECTROGRAFTING OF ARYLDIAZONIUM SALTS.

Frédéric Kanoufi,[1] Sorin Munteanu,[a] Yasmina Fedala,[a,b] Cécile Flammier,[c] Jean-Paul Roger,[b] Gilles Tessier,[b] Fabien Amiot,[c] Catherine Combellas,[a]

[a] *Physicochimie des éllectrolytes, des colloides et sciences analytiques, CNRS UMR 7195, ESPCI-Paris Tech, 10 rue Vauquelin, 75231,Paris Cedex 05*
[b] *Institut Langevin / ESPCI ParisTech / CNRS UMR 7587, Laboratoire d'Optique Physique, 10 rue Vauquelin, 75231 Paris Cedex 05*
[c] *Insitut FEMTO-ST, CNRS-UMR 6174 / UFC / ENSMM / UTBM, 24 chemin de l'Epitaphe, 25030 Besançon, France*

The detection of local fluxes of matter or the measurement of the local reactivity of interfaces is a challenge in different fields of micro or nanosciences, for example to follow the local activity of biological cells or the catalytic properties of nanostructured materials. One approach, based on local probes microscopies, consists of scanning a probe above a surface to interrogate its local physical and/or chemical properties. Indeed, Scanning Electrochemical Microscopy based on microelectrodes tips allows probing the local (electro)chemical heterogeneity of various interfaces.

Another approach consists of coupling an electrochemical measurement to a local optical detection, owing to a microscopy imaging technique. Very recently, Surface Plasmon Resonance (SPR) allowed detecting the heterogeneity of a charge transfer reaction at an electrode (1). Although highly sensitive, SPR imagery requires constrained experimental conditions and instead, we propose a more versatile method. It consists of coupling the electrode activation to the local change of its refractive index by imaging its optical reflectivity. Here, the reflectivity setup will be used i) to study the reaction mechanism for surface electrografting by reduction of aryldiazonium salts (2) and ii) to characterize the local (electro)chemical reactivity of surfaces.

Reflectance images allow characterizing *in situ* and in real time the kinetics for the growth of the electrografted organic film with a 1 nm thickness resolution and a < 1 µm^2 spatial resolution. The potentialities of this technique for imaging are illustrated in Figures 1 and 2. The method is particularly suited for microfluidics, as illustrated in Figure 1 where the selective electrografting reaction onto band microelectrodes arrays (5 µm x1 mm) is evidenced. The film growth may also be studied on locally passivated surfaces obtained by micro contact printing of different moieties. For example, with a gold surface printed by BSA (bovine serum albumin) electrografting of nitrobenzenediazonium is performed selectively onto pristine regions (dark zones in Fig. 2). This allows quantifying the chemical reactivity of electrogenerated radicals toward different molecular species.

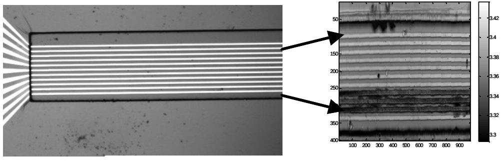


Figure 1

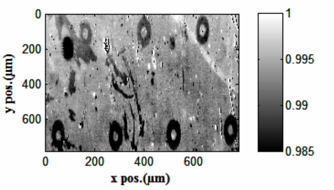


Figure 2

Reference:

(1) Tao N. and coll. *Science* **2010**, *327*, 1363.
(2) Pinson, J.; Podvorica, F. *Chem.Soc.Rev.* **2005**, 34, 429.

Note OC-3 :

ELECTROREDUCTION OF DIAZONIUM SALTS IN AQUEOUS MEDIUM VIA HOST –GUEST COMPLEXATION AND THE FORMATION OF MIX MULTIFUNCTIONAL ORGANIC MATERIALS

Luis Santos, Jalal Ghilane, Pascal Martin, Gaëlle Trippé, Hyacinthe Randriamahazaka, Jean-Christophe Lacroix

ITODYS, CNRS UMR 7086, Université Paris Diderot, 15 rue Jean de Baif, 75205 Paris, France
luis.santos@jussieur.paris7.fr

The functionalization of surfaces through the covalent attachment of organic monolayers is the subject of intense attention due to the numerous potential applications of controlled and stable organic/metal interfaces. The scope of these investigations covers large fields in molecular electronics, chemistry, and bioanalytical chemistry, going from the preparation of monolayer surface insulators to the incorporation of chemical/biochemical functionality at interfaces for use in photovoltaic conversion or the development of new chemical/biological sensing devices.(1) Concerning the immobilization of organic molecules onto the surface, the convenient reaction is certainly the electrochemical grafting associated with the reduction of aryldiazonium salt.(2) We will present in this work the electrochemical grafting of an organic layer, the bisthiophenebenzene BTB, encapsulated in β-cyclodextrin (β-CD) aqueous solution.(3) Moreover, we will discuss about the possibility of selectively remove the β-CD by the simplest immersion of the electrode into organic solvent leading to the patterning of the surface by the BTB. In addition we will show the reversibility of the encapsulation of the BTB with the β-CD. The attachment of the encapsulated organic layer to the carbon electrode in aqueous solution and the patterning of the surface by BTB, after removing the β-CD, will be investigated using cyclic voltammetry (CV), scanning electrochemical microscopy (SECM), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Finally we will discuss the possibility to feel out the patterned surface, after removing the β-CD, by the electrodeposition of another organic material, i.e. another diazonium, in order to generate a new kind of tunable mix organic material. Such substrates could be used for electrocatalysis, optical and electronic devices.

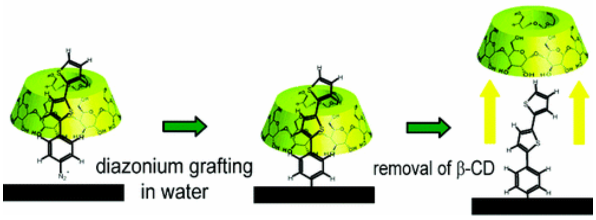


Fig 1: electrochemical grafting of an organic layer, the bisthiophenebenzene BTB, encapsulated in β-CD.

Reference:

(1) Buriak, J. M. *Chem. Rev.* **2002**, 102, 1271-1308.
(2) Ghilane, J. Delamar, M. Guilloux-Viry, M. Lagrost, C. Mangeney, C. Hapiot, P. *Langmuir*. **2005**, 21(14), 6422-6429.
(3) Santos, L.; Ghilane, J.; Martin, P.; Lacaze, P-C.; Randriamahazaka, H.; Lacroix, J-C. *J.A.C.S.* **2010**, 132 (5), 1690-1698.

Note OC-4 :

POLYMER BRUSHES AND THEIR APPLICATION IN CHARGE TRANSPORT PROCESSES

Mie Lillethorup, [a,b] Joseph Iruthayaraj, [a] Sergey Chernyy, [a] Marcel Ceccato, [a] Peter Kingshott, [c] Flemming Besenbacher, [c] Mogens Hinge, [a] Steen Uttrup Pedersen, [a,c] and Kim Daasbjerg [a,b,c]

[a] *Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark*
[b] *Center for Oxygen Microscopy and imaging (COMI), Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark*
[c] *Interdisciplinary Nanoscience Center (iNANO), Institute of Physics and Astronomy, Ny Munkegade, DK-8000 Aarhus C, Denmark*

Modification of surfaces by polymers has become a field of increasing interest due to its many applications. Polymer brushes formed by surface initiated polymerization, such as atom transfer radical polymerization (ATRP), result in densely packed and strongly bound surface films. In addition, a high degree of order characterizes these polymer layers, which for example can be used in the study of charge-transporting phenomena in electronic devices.

In this work we have studied the surface-initiated ATRP of methyl methacrylate from surfaces modified with a diazonium-based ATRP-initiator containing a tertiary alkyl bromide functionality.[1] The different parameters such as the bromine content of the initiator layer, polarity of reaction medium, ligand type, and the ratio of activator (Cu^I) to deactivator (Cu^{II}) have been varied in order to optimize the controllability of the polymerization. Interestingly, very thick polymer brushes, on the order of 1 μm, could be obtained at high bromine content of the initiator layer.

Most recently, we have investigated charge-transport through poly(ferrocenylmethyl methacrylate) brushes. The surface films are characterized by electrochemical techniques as well as by ellipsometry, X-ray photoelectron spectroscopy (XPS), and polarization modulation-infrared reflection absorption spectroscopy (PM-IRRAS). By means of the scanning electrochemical microscopy (SECM) technique, patterns of polymers could be created for these systems.

Reference:

(1) Iruthayaraj, J.; Chernyy, S.; Lillethorup, M.; Ceccato, M.; Røn, T.; Hinge, M.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *Langmuir* **2010**, *27*, 1070-1078.

Note OC-5 :

ELECTROCHEMICAL DEPROTECTION AND ACTIVATION OF MICHAEL ACCEPTORS FOR ELECTRODE MICROSTRUCTURATION.

Jan Clausmeyer,[a] Joerg Henig,[a] Nicolas Plumeré,[a] and Wolfgang Schuhmann[a]

[a] *Ruhr Universität Bochum, Center for Electrochemical Science, Universitätsstrasse 150, 44780, Bochum, Germany.*

The development by directed evolution of O_2-tolerant Fe-Fe-hydrogenases as biocatalysts for semi-artificial H_2-producing systems[1] requires the characterization of tens of thousands of proteins. Biochip technologies are extremely powerful for high-throughput screening of biocatalysts. One single chip may be loaded with 10^6 of different probes and individually addressed via electrochemical tools. An efficient method for the attachment and patterning of proteins on surfaces is crucial to the construction of such protein chips. The main limitations in biochip fabrication are related to the unspecific protein binding and denaturation of the adsorbed proteins upon subsequent protein attachment.

In the present work, catechols and parahydrochinone protected as tert-buytldimethylsilyl ethers (TBDMS) are immobilized on electrode surfaces. The cleavage of the TBDMS groups as well as the oxidation to the chinone are controlled electrochemically. The chinones are employed as Michael acceptor for the reaction with nucleophilic groups (amines and thiols) from the redox proteins. The electrochemical control of the deprotection and activation of the chinone allows for local modification of the electrode surface.

The presence of the TBDMS groups prevents the unspecific binding of biomolecules in the non-activated electrode areas. Moreover, the Michael addition takes place upon local electrochemical activation without affecting the redox molecules already immobilized. This makes the serial patterning of proteins possible, which is essential to the preparation of protein chips.

Scanning electrochemical microscopy (SECM) was applied for both the microstructuration of the electrode surface with the biocatalyst component (writing) and the signal detection (reading).

Reference:

(1) Stripp, S., Goldet, G., Brandmayr, C., Sanganas, O., Vincent, K. A., Haumann, M., Armstrong, F. A. and Happe, T., *PNAS,* **2009,** *106*, 17331-17336.

Note OC-6 :

GROWTH OF POLYMER BRUSHES INITIATED FROM A SURFACE FUNCTIONALIZED BY CONDUCTING POLYMER.

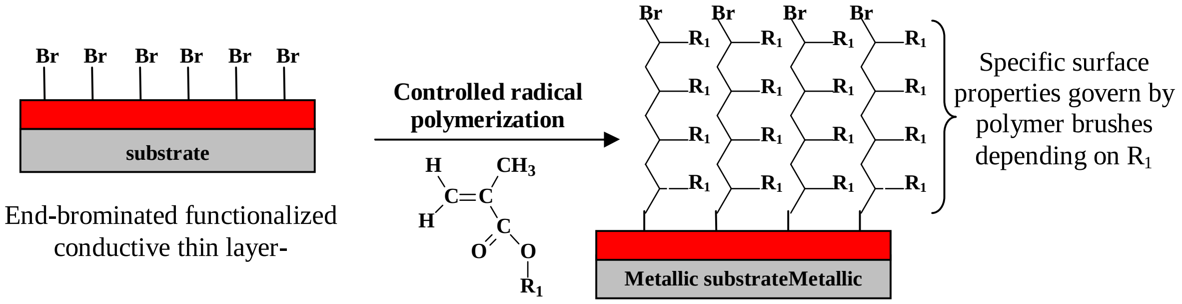
Christian PERRUCHOT, Amani CHAMS, Gregory DUPEYRE and Mohamed JOUINI.

Laboratoire ITODYS, Université Paris Diderot - Paris 7, UMR 7086,
15, rue Jean de Baïf, 75205 Paris Cedex 13 (France).

Polymer brushes covalently grafted onto a surface can be used as a support to serve in many applications that require an important interfacial surface's area, such as heterogeneous catalysis or chemical- / biochemical- sensors. However, when polymer brushes are grafted to a surface, generally they inhibit its conductive properties and thus limit their interest for such applications [1]. Therefore, it is important to obtain conductive final material formed by a polymer brushes layer having specific properties at surface directly grafted onto a conducting polymer layer deposited on a substrate. Moreover, depending on the specific properties of the polymer brushes, the surface properties of resulting material can be designed on demand.

In this work, we succeeded to grow polymer brushes directly from metallic surface, on which a functionalized conductive polymer thin layer was previously electrodeposited. The conductive polymer layer is based on pyrrole-thiophene-pyrrole monomer N-functionalized by an end-brominated alkyl side chain. The terminal bromide atom of the pendent chain subsequently served to grow polymer brushes using Atom Transfer Radical Polymerization (ATRP) of N, N dimethyl amino ethyl methacrylate monomer [2]. The radical polymerization initiated from functionalized conductive layer deposited on surface substrate leads to covalently linked polymer brushes with controlled thickness. The resulting modified electrode device corresponds to a multi-component layers material exhibiting conducting properties covered by dense polymer brushes having large surface contact with specific properties depending on the nature of lateral groups R_1 (See Scheme below).

In this presentation, we show that the conductive thin polymer layer remains conductive and only the rate of electronic transfer is modified despite the grafting of highly dense polymer brushes; and that the specific properties of the external polymer brushes layer govern the surface properties of the final material.



References:

(1) H. S. Nalwa, Handbook of Organic Conductive Molecules and Polymers, Volume 2, Conductive Polymers: Synthesis and Electrical Properties, 1997, John Wiley & Sons.

(2) K. Matyjaszewski and J. Xia, « Atom Transfer Radical Polymerization », Chem. Rev., 2001, 101, 2921-2990.

Note OC-7 :

ELECTROCHEMICALLY-ASSISTED DEPOSITION OF SOL-GEL MATERIALS: NANO-STRUCTURATION AND MODIFICATION OF NANO-OBJECTS

Mathieu Etienne, A. Walcarius

LCPME, UMR CNRS-NANCY Université,
405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, FRANCE
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The sol-gel process provides unique opportunity to produce hybrid materials combining simultaneously organic and inorganic properties in a single solid [1]. In addition, the porosity of such materials can be tuned and the shape of the solid can be adapted to the application, from monolith to particles and thin films. For these reasons sol-gel materials have found applications in various fields such as (bio)sensors, corrosion protection and energy production or storage [1,2]. Recently, the possibility to assist electrochemically the deposition of sol-gel materials has triggered new developments at the interface between electrochemistry and sol-gel chemistry [3].

In electrochemically-assisted deposition (E-AD) an electrochemical modulation of pH at the electrode/electrolyte interface induces a rapid gelification reaction only at the electrode surface and the formation of a thin sol-gel film. We would like here to give an overview of our activities in the field by showing some possibilities offered by E-AD for electrode surface functionalization [4,5], thin film nanostructuration [6,7], bio-encapsulation [8,9] and controlled modification of nano-objects [10,11]. We will also show that E-AD can be applied to the local modification (or patterning) of a surface with a scanning electrochemical microscope (SECM), where the process is only limited by the size of the electrode [12].

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Note OC-8 :

TUESDAY 24 MAY

9:00 – 9:45 : IL2

M. Grätzel

Nanocrystalline junctions and mesosocopic solar cells

9:50 – 10:10 : OC 09

Rutkowska

Development and evaluation of inorganic charge mediators for dye sensitized solar cells

10:10 – 10:30 : OC 10

N. Vlachopoulos

Electron hopping across molecules adsorbed at the nanostructured oxide-electrode interface and its relevance to dye sensitised solar cells

10:30 – 11:00

Coffee break

11:00 – 11:20 : OC 11

S. Ahmad

Poly(thiophenes) based highly efficient counter electrodes for Dye-sensitized solar cell applications

11:20 – 11:40 : OC 12

U. Tefashe

High resolution imaging of dye-sensitized solar cell electrodes with scanning electrochemical microscopy

11:40 – 12:00 : OC 13

J. Elias

Electrochemical deposition of order urchin-like ZnO nanostructures and their application in Extremely Thin Absorber Solar cells

12:00 – 12:20: OC 14

V. Guerin

Electrodeposited Nanoporous versus Nanoparticulate ZnO Films of Similar Roughness for Dye-Sensitized Solar Cells.

NANOCRYSTALLINE JUNCTIONS AND MESOSOCOPIC SOLAR CELLS

Michael Grätzel

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The field of photovoltaic cells has been dominated so far by solid state p-n junction devices made e.g. of crystalline or amorphous silicon or other chalcogenide semiconductors, profiting from the experience and material availability of the semiconductor industry. However, there is an increasing awareness of the possible advantages of devices referred to as “bulk” junctions due to their interconnected three-dimensional structure. Their embodiment departs completely from the conventional flat p-n junction solid-state cells, replacing them by interpenetrating networks. This lecture focuses on dye sensitized and quantum dot sensitized mesoscopic solar cells (DSCs), which are leading this new generation of photovoltaic devices [1-4]. Imitating the light reaction of natural photo-synthesis, this cell is the only photovoltaic system that uses molecules to generate charges from sunlight accomplishing the separation of the optical absorption from the charge separation and carrier transport processes. It does so by associating a molecular dye with a nanocrystalline film of a large band gap semiconductor oxide. The DSC has made phenomenal progress, present conversion efficiencies being over 12 percent for single junction and 17 percent for tandem cells. The validated module efficiency has reached 10 percent, rendering the DSC a credible alternative to conventional thin film p-n junction devices. Commercial large-scale production of flexible DSC modules has started in 2009. These solar cells have become viable contenders for large-scale future solar energy conversion systems on the bases of cost, efficiency, stability and availability as well as environmental compatibility.

Reference:

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4) M.Grätzel, *Acc. Chem. Res*. 42, 1781-1798 (**2009**).

Note IL-2 :

DEVELOPMENT AND EVALUATION OF INORGANIC CHARGE MEDIATORS FOR DYE SENSITIZED SOLAR CELLS

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Successful application of mesoporous anatase TiO_2 films in dye-sensitised solar cells (DSSCs) caused a wide-spread interest in the properties of this new category of porous nanocrystalline semiconducting electrodes. The mesoporosity and nanocrystallinity of the semiconductor are important factors not only because of the possibility of large amount of dye to adsorb on the very large surface area but also for two additional reasons. The nanostructured morphology allows the semiconductor small particles to become almost totally depleted upon immersion in the electrolyte (allowing for large photovoltages), and the proximity of the electrolyte to all particles makes screening of injected electrons, and thus their transport, feasible. Nonporous TiO_2 film texture is also of importance when it comes to anchoring photosensitizer (here N3 dye, i.e. cis – dithiocyanoatobis (4,4'-dicarboxylic acid-2,2'-bipyridine) ruthenium(II)) at quasi-monolayer level to ensure efficient light – harvesting and electron injection.

Redox mediators (charge relays) are used to ascertain regeneration of dyes. An effective system should be in principle, a fast redox conducting material characterized by a formal potential close to the ground state of the dye used. Although alternative redox couples to I^-/I_3^- have also been developed and successfully applied in DSSCs, so far I^-/I_3^- has proven to be the most efficient redox couple for high efficiency. In the present work, we propose to utilize metal hexacyanoferrates, interesting group of polynuclear inorganic compounds as mediators for DSSC. Metal hexacyanoferrates are very well-definite inorganic materials and they represent an important class of mixed-valence compounds, of which Prussian Blue is the classical prototype. Metal hexacyanoferrates are also good ionic (K^+) conductors, and they have zeolite character. These compounds are characterized by chemical and mechanical stability. Their redox reactions are fast and reversible. Charge transport occurs by electron hopping. Metal hexacyanoferrates also exhibit electrocatalityc, electrochromic, ion-exchange and photomagnetic properties. The representative example, nickel(II) hexacyanoferrate(II,III), that is considered in the present work seems to be particularly attractive for DSSC because, although its potential is still more negative relative to the dye's ground state, the potential is more positive in comparison to the I_3^-/I^- couple.

Note OC-9 :

OC-10

ELECTRON HOPPING ACROSS MOLECULES ADSORBED AT THE NANOSTRUCTURED OXIDE-ELECTRODE INTERFACE AND ITS RELEVANCE TO DYE SENSITISED SOLAR CELLS

Nikolaos Vlachopoulos,[a] Gerrit Boschloo[a], Erik Carlsson[a], Erik Gabrielsson[b], Leif Haeggman[a], Anders Hagfeldt[a], Licheng Sun[b], and Marcelo Zuleta[a]

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[b] *School of Chemical Science and Engineering, Department of Chemistry, Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden*

Dye-sensitised solar cells have attracted a lot of interest in the last 25 years, and the physical chemistry at the interface between dye-coated oxide and electrolyte is an active field of research[1]. The dye support is a nanoparticulate porous layer of 5-15µm thickness supported on conductive transparent glass, on which the dye is chemisorbed via an appropriate attachment group, commonly carboxylate or phosphonate. At electrode potentials more positive than the value corresponding to the conduction band edge of the semiconductor no electron transfer is expected between dye and conducting glass support of the oxide due to the insulating properties of the oxide. However, electron hopping (lateral electron transfer) across the chemisorbed dye layer is possible in several cases, so that faradaic current flow is observed from dye to conducting glass support and vice versa[2]. In this presentation, both traditional ruthenium coordination dyes and novel metal-free organic dyes with a triphenylamine moiety covalently linked to a cyanoacrylic acid are studied by cyclic voltammetry and impedance spectroscopy. The oxidation current is correlated to the amount of adsorbed dye so that the onset of electron hopping is evidenced above a critical dye surface concentration threshold due to the necessity of close proximity between adsorbed dye molecules (percolation effect). With respect to the time scale of the voltammetric experiments transition between diffusion limitation and quasi-Nernstian behaviour is evidenced from the dependence of peak current on scan rate. Electron hopping at oxide electrodes is analogous to that at other types of chemically modified electrodes and, apart from implications in dye solar cell operation e.g. as regards the enhancement of the dark current, it is of potential interest to applications of oxide-based electrodes in various areas of electrochemical technology, e.g. electrochromics, electrocatalysis and sensors.

References:

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Note OC-10 :

OC-11

POLY(THIOPHENES) BASED HIGHLY EFFICIENT COUNTER ELECTRODES FOR DYE-SENSITIZED SOLAR CELL APPLICATIONS

Shahzada Ahmad,[a,b] Jun-Ho Yum,[b] Hans-Jürgen Butt,[a] Michael Grätzel [b], Mohammad K. Nazeeruddin,[b]

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Ionic liquids are molten salts which acts as ready to use electrolytes, can produce unparallel structural variation with robust cycling life when use a media for electrodeposition. Ionic liquids are electrochemically stable and now regarded as a ‘‘designer solvent’’ to cater the future need of electrochemical challenges and process. As a consequence they are ideal solvents for a range of electrochemical processes that are otherwise difficult or impossible to study. Many different materials can be electrodeposited from ionic liquids including metals and conducting polymers in a cost effective way directly on the electrodes. These materials are useful for energy storage and conversion devices, catalysts and actuators.

The realization of stable π-conjugated polymer based electrochemical devices remains a difficult goal because of performance limitations that include poor environmental stability and redox properties. By the use of ionic liquids as a growth media one can easily alter the growth conditions at electrode-electrolyte interface to produce grains in the nanometer scale. Ionic liquids are excellent media for electropolymerization of conducting polymers, and can exercise strong influence on chemical or physical properties. This will orchestrate the formation of nanoporous films with uniform and adherent layers on any conducting electrode.

For example poly(3,4-ethylenedioxythiophene) [PEDOT] and its analogous can produce, nanoporous layers when electropolymerized in ionic liquids. This allows the fabrication of platinum free highly efficient dye-sensitized solar cells, at a fraction of the cost of platinized electrode without any loss on power conversion efficiencies. Thin layers of PEDOT have reasonably high electrocatalytic properties and low charge transfer resistance than platinum along with very high cycling life. This approach can be easily exploited to fabricate poly(thiophenes) and provide an avenue for applications requiring stable redox polymers in energy devices [1,2].

References:

(1) S. Ahmad, J.-H Yum, Z. Xianxi, M. Grätzel, H.-J. Butt, M. K. Nazeeruddin, J. Mater. Chem., **2010**, 20, 1654.
(2) S. Ahmad, J.-H Yum, H.-J. Butt, M. K. Nazeeruddin, M. Grätzel, ChemPhysChem, **2010**, 13, 2814.

Note OC-11 :

HIGH RESOLUTION IMAGING OF DYE-SENSITIZED SOLAR CELL ELECTRODES WITH SCANNING ELECTROCHEMICAL MICROSCOPY

Ushula Mengesha Tefashe,[a] Melanie Rudolph,[b] Derck Schlettwein,[b] Gunther Wittstock[a]

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[b] *Institute of Applied Physics, Justus Liebig University of Gießen, Heinrich-Buff-Ring 16, D-35392 Gießen, Germany*

Porous dye-sensitized solar cell electrodes were imaged under both illuminated and non-illuminated conditions using scanning electrochemical microscopy (SECM) with shearforce based tip-substrate distance control. The system is capable to acquire high resolution topographic images of the samples together with the map of electrochemical signals [1-3]. At the dye-sensitized electrode under illumination we considered electrochemical reactions associated with the electrolyte species (I^-/I_3^-) and photo-oxidized dye to map the inhomogeneity in localized photoelectrochemical activity. Locations that possessed non-uniform SECM probe currents under illuminated conditions compared to constant current over non-illuminated surface were visualized. The study was directed to investigate the relationship between structure and function of dye sensitized nanoporous metal oxide grains with nanoscale resolution. The interpretation is supported by atomic force microscopy (AFM) images showing topography of the same region on the sensitized film.

References:

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Note OC-12 :

OC-13

ELECTROCHEMICAL DEPOSITION OF ORDER URCHIN-LIKE ZNO NANOSTRUCTURES AND THEIR APPLICATION IN EXTREMELY THIN ABSORBER SOLAR CELLS

Jamil Elias,[a] Mikhael Bechelany,[b] Ivo Utke,a Johann Michlera and Laetitia Philippea

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b *Institut Européen des Membranes de Montpellier (UMR CNRS 5635) Place Eugène Bataillon 34095 Montpellier, France*

Ordered arrays of 1D single-crystal ZnO nanowires have emerged as promising buildingblocks for a new generation of devices in different technological domains such as optoelectronics, solar cells, gas sensing, field emission and piezoelectrics. Among the various deposition techniques, electrochemical deposition appears as a versatile method and well suited to synthesize ZnO [1] with a large variety of morphologies and dimensions [2-4]. What is now a relevant area of focus in nanoscience involves the preparation of higher-order assemblies, arrays, and superlattices of these 1D nanostructures. Hollow urchin-like ZnO NWs that combine properties of 3D and 1D materials may emerge as a more interesting alternative than simple arrays of NWs due to the higher specific surface especially for application in dye and semiconductor-sensitized solar cells.

In this contribution, we will present an original and new approach to fabricate, at a time scale compatible with large-scale production, thin films composed of well-ordered urchin-like ZnO nanowires (NWs) hollow from inside (Figure 1a and b) and with controlled NWs and core dimensions. The synthesis method combines the formation of a polystyrene microsphere monolayer and the electrodeposition of ZnO NWs, followed by the elimination of the microspheres, which play the role of a template [5]. The dimensions of the NWs can be controlled by varying the composition of the electrolyte. Furthermore, an additional step enabling the control of the interdistance between the nanostructures will be shown. The geometry and interdistance effects on the light diffusion as well as preliminary results on extremely thin absorber (ETA) solar cells based on ZnO/CdSe/CuSCN will be presented (Figure 2).

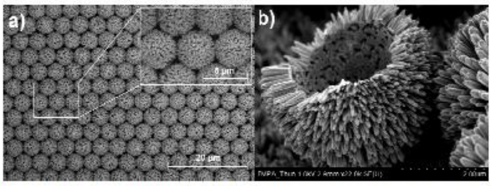

Fig. 1 SEM images of: a) hollow ordered urchin-like ZnO NWs deposited on TCO substrate, the inset represents a higher magnification image, b) Mechanically broken individual urchin structure.

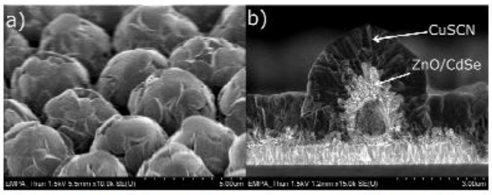

Fig. 2 a) Tilted and b) cross sectional SEM images of ZnO/CdSe/CuSCN ETA solar cell based on ZnO urchin structures.

References:
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(5) Elias, J; Lévy-Clément, C.; Bechelany, M; Michler, J.; Wang, G.Y.; Wang, Z.; Philippe, L. *Adv. Mater.* **2010**, *22*, 1607.

Note OC-13 :

OC-14

ELECTRODEPOSITED NANOPOROUS VERSUS NANOPARTICULATE ZNO FILMS OF SIMILAR ROUGHNESS FOR DYE-SENSITIZED SOLAR CELLS.

Victoire-Marie Guérin,[a] Thierry Pauporté,[a] Constance Magne,[a] Tangui Le Bahers,[a]
Jiri Rathousky [b]

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[b] *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 18223 Prague 8, Czech Republic.*

Zinc oxide has recently emerged as a promising alternative semiconductor material to TiO_2 with marked performance improvements of ZnO-based DSSCs (dye-sensitized solar cells) achieved during the last few years.[1-3] We present a comparative study of two different ZnO porous film morphologies for dye-sensitized solar cell (DSSC) fabrications. Nanoparticulate ZnO were prepared by doctor-blade starting from a paste containing ZnO nanoparticles. Nanoporous ZnO films were grown by a soft template-assisted electrochemical growth technique. The film thicknesses were adjusted at similar roughness of about 300 in order to permit a worthy comparison.

The effects on the cell performances of sensitization by dyes belonging to three different families, namely, xanthene (eosin Y) and indoline (D102, D131, D149 and D205) organic dyes as well as a ruthenium polypyridine complex (N719), have been investigated. The mesoporous electrodeposited matrix exhibits significant morphological changes upon the photoanode preparation, especially upon the dye sensitization, that yield to a dramatic change of the inner layer morphology and increase in the layer internal specific surface area. In the case of indoline dyes, better efficiencies were found with the electrodeposited ZnO porous matrices compared to the nanoparticulate ones in spite of significantly shorter electron lifetimes measured by impedance spectroscopy. The observation is interpreted in terms of much shorter transfer time in the oxide in the case of the electrodeposited ZnO films. Among the tested dyes, the D149 and D205 indoline organic dyes with a strong acceptor group were found the most efficients with the best cell over 4.6% of overall conversion efficiency.[3]

References:

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(2) Le Bahers, T.; Labat, F.; Pauporté, T.; Ciofini I. *Phys. Chem. Chem. Phys.*, **2010**, *12*, 14710–14719.
(3) V.M. Guérin, C. Magne, T. Pauporté, T. Le Bahers and J. Rathousky, *ACS Appl. Mater. Interfaces* **2010**, *2,* 3677–3685.

Note OC-14 :

TUESDAY 24 MAY

14:00 - 14:45: IL3

R. Zeissel

New Luminescent Organic Dyes around a Boron Center: Synthesis and Optical Applications

14:50 - 15:10: OC 15

P. Lainé

Designing Multifunctional Expanded (Bi-) Pyridiniums: Electrochemical Properties of Branched and Fused Derivatives

15:10 – 15:30: OC 16

J. Ludvik

Organic molecules of the "push-pull" type with a systematically extended π-conjugated bridging system

15:30 – 15:50: OC 17

Y. Zholudov

Electrochemiluminescence of Doped Nanoordered Organic Films

15:50 – 16:30
Coffee break

16:30 – 16:50 : OC 18

Taleb

Shape-Controlled Electrodeposition of Metal Nanostructures Trough Using Self Assembled Fonctionalized Gold Nanoparticle Template

16:50 – 17:10 : OC 19

P. Ugo

Recent advances in the preparation and electrochemical use of ensembles of nanolectrodes: from 2-D surfaces to 3D hierarchical nanostructures

17:10 – 17:30 : OC 20

L. Bouffier

Direct Conversion of Energy by Chemically Powered Micro-motors

17:30 – 17:50 : OC 21

Da Pozzo

Photo-catalytic behaviour of self-organized TiO_2 nanotubes prepared in organic electrolytes

17:50 – 18:10 : OC 22

V. Bonometti

Genetically modified” spider-like oligothiophenes: Electron properties and polymerization ability

NEW LUMINESCENT ORGANIC DYES AROUND A BORON CENTER: SYNTHESIS AND OPTICAL APPLICATIONS

Raymond Ziessel

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Several sets of borondipyrromethene (BODIPY) dyes have been synthesized in such a way that the central fluorescent unit bears one or more appended aromatic polycycles. These latter units function as ancillary light-harvesters and channel incident photons to the BODIPY emitter. The detailed mechanisms of intramolecular energy transfer have been elucidated on the basis of steady-state and time-resolved spectroscopic measurements and related to the geometry of the assembly. It is noteworthy that the attached polycycle serves to enhance the virtual Stokes shift, to introduce a means to form well-organized thin films, and to render the compound subject to transport charges. In certain cases, this latter effect can lead to self-association into organised structures that absorb and emit at long wavelength. The novelty of these new dyes relates to the substitution pattern and most notably the replacement of the usual fluorine atoms with aromatic polycycles. In the extreme case, multiple substitution leads to arrays bearing different polycycles that absorb over much of the visible spectral window and transfer photons to the BODIPY centre within a few picoseconds.

Separate synthetic protocols allows the tuning of colours of these dyes from yellow to green but also the fluorescence from green to red and to the NIR. Separate studies indicate that the BODIPY dye will enter into intramolecular charge-transfer reactions with attached redox-active groups. Such realisations have led to the development of fluorescence sensors for substrates from solution and to write / read / erase devices. Subsequent charge recombination provides an easy means by which to populate the triplet excited state resident on the BODIPY core, despite the realisation that intersystem crossing is extremely inefficient in the absence of charge-transfer effects.

The two processes light harvesting and charge transfer, can be accommodated in the same structure by suitable synthetic strategies. Here, rapid energy transfer occurs from the appended aromatic polycycle to the BODIPY unit and is followed by fast charge transfer to the redox-active component. Highly versatile arrays can be generated in this way that operates as artificial photosynthetic and light emitting devices.

Applications in dye sensitized bulk heterojunction solar cells, OLEDs and fluorescent liquid crystals will be scrutinized.

References:

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T. Rousseau, A. Cravino, T. Bura, G.
Ulrich, R. Ziessel, J. Roncali, *Chem. Commun*, 2009, 1673. T. Rousseau, A. Cravino, T. Bura, G. Ulrich, R. Ziessel,J. Roncali, *J. Mater. Chem*. **2009**, *19*, 2298-2300.

Note IL-3 :

OC-15

DESIGNING MULTIFUNCTIONAL EXPANDED (BI-) PYRIDINIUMS: ELECTROCHEMICAL PROPERTIES OF BRANCHED AND FUSED DERIVATIVES

Philippe P. Lainé,[a] Jérôme Fortage,[a] Fabien Tuyèras,[a] Sophie Griveau,[b] Fethi Bedioui,[b] Francesco Nastasi,[c] Fausto Puntoriero,[c] Sebastiano Campagna,[b] Cyril Peltier,[d] Ilaria Ciofini[d] and Carlo Adamo[d]

[a] Laboratoire ITODYS, CNRS UMR-7086, Université Paris Diderot, Bâtiment Lavoisier, 15, rue Jean Antoine de Baïf, F-75205 Paris Cedex 13, France
[b] Unité de Pharmacologie Chimique et Génétique et d'Imagerie, CNRS UMR-8151 and INSERM U-1022, Université Paris Descartes, ENSCP – Chimie ParisTech, 11 rue P. et M. Curie, F-75231 Paris Cedex 05, France
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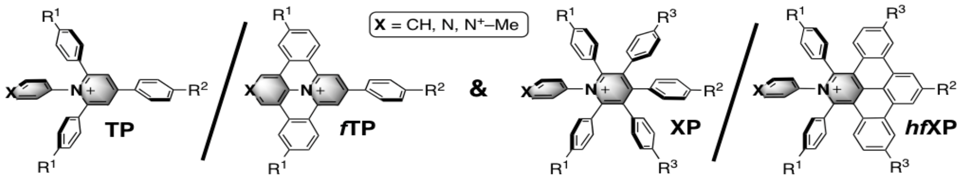
As part of our continuing research program devoted to Artificial Photosynthesis, with the aim of producing photoinduced charge-separated states within semi-rigid pyridinium-based inorganic dyads,[1] we have recently revisited both the (photo)chemistry and the physical chemistry of mono- and oligo-pyridinium electron-accepting species.[2] Here we report on the multifaceted properties of so-called expanded pyridiniums (EPs) comprised of two subclasses (see Figure): the *branched* EPs (i.e. polyaryl-substituted pyridiniums of types **TP** and **XP**) and their *fused* or *hemi-fused* counterparts (types ***f*TP** and ***hf*XP**, respectively).



From insights we gained from the cross experimental-theoretical study of EPs of the first generation (X = CH in Figure), we derived a strategy to design novel multifunctional bipyridiniums (X = N and N$^+$–Me in Figure) behaving not only as good electrophores, but also as good chromophores and good luminophores.[2] Amongst the different electrochemical behaviors observed for these (bi)pyridiniums, the intriguing capability to undergo bielectronic reduction at a single potential is of particular interest. Indeed, controlling multielectron processes at the molecular level is a key requirement for the photochemical conversion of (solar) energy. The appealing features of the new EPs are presented and discussed here.

References:

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Note OC-15 :

ORGANIC MOLECULES OF THE "PUSH-PULL" TYPE WITH A SYSTEMATICALLY EXTENDED π-CONJUGATED BRIDGING SYSTEM

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Organic molecules with readily polarisable push-pull electronic systems are attractive as tunable chromophores for nonlinear optics (NLO) having broad application as two-photon absorbing devices, opto-electronic and optical data storage devices, organic light-emitting diodes (OLED) or organic photovoltaic cells. A typical organic D-π-A chromophore consists of strong electron acceptors - A (e.g. NO_2 or CN groups) and donors - D (e.g. NR_2 or OR groups) connected by a π-conjugated system. [1]. Recently, several new series of imidazole derivatives (about 50 compounds) were synthesized and basic electrochemical and spectrometric characterisation has been performed [2,3,4].

A part of the substances are based on 4,5-dicyanoimidazole acceptor and dimethylamino donors connected by systematically enlarged π-conjugated spacer. The other part of compounds contains 4,5-*bis*(dimethylanilino) imidazole unit as a donor and various acceptors combined with extended bridge.

For fundamental electrochemical characterization polarography, cyclic voltammetry (CV) and rotating-disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile, N,N-dimethylformamide) has been used.

Due to multiple redox centres present, the molecules exhibit several redox processes. From the aspect of NLO, the attention has been paid mainly to the first oxidation and first reduction process that should be reversible, involving one transferred electron. The influence of different linker has been followed and a mixed influence of length and planarity was found and discussed. The difference between the first oxidation and reduction potential was correlated with the HOMO-LUMO gap and with the spectral properties (colour) of the substance. The most suitable chemical compositions were selected and the more general rules discussed.

Acknowledgement: Financial support from the Ministry of Education, Youth, and Sports of the Czech Republic (No. MSM0021627502 and Project No. LC 510) is gratefully acknowledged. The authors thank Assoc. Prof. Filip Bureš for synthesis of examined organic compounds.

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Note OC-16 :

ELECTROCHEMILUMINESCENCE OF DOPED NANOORDERED ORGANIC FILMS

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Since the development of organic optoelectronic devices including light emitting diodes and solar cells there arouse the need in studying excitation, energy and charge transfer processes in thin organic films of different composition. One of the methods for obtaining such information is the electrogenerated chemiluminescene (ECL) [1]. In the framework of this method application the working electrode of ECL cell is covered by appropriate organic film that is put in contact with electrolyte solution. The electrolyte solution contains either some reversible redox active species charged at the counter electrode or species charged at the film modified working electrode with the following chemical transformation (so called coreactants). The later are taking part in ECL emitters' formation.

In this work we have studied the ECL response of indium-tin oxide electrodes covered with the nanoordered Langmuir-Blodgett (LB) films of polymethylmethacrylate (PMMA) doped with organic luminophors using coreactants. PMMA served as an insulating matrix used for LB film formation. The films contained organic luminophors rubrene and 9,10-diphenylanthracene that do not form the film themselves. Though the LB technique is rather time-consuming and laborious procedure comparing with other methods like spin-coating it allows precise control of film thickness, composition and structure. Thus essential advantages are obtained for studying mechanisms of processes within such films.

The linear potential sweep in the anodic range was applied to the working electrode. The ECL excitation was done using two coreactants – the known tripropylamine and recently reported tetraphenylborate (TPB) anion [2]. Use of TPB anion as a coreactant gives efficient and reproducible ECL emission from the studied films during their oxidation. The observed ECL intensity is comparable to that obtained with tripropylamine coreactant. At the same time TPB ion possesses certain advantages over the later, i.e. TPB salts are nonvolatile. That considerably simplifies ECL experiments when solution bubbling with inert gas is required. It is also much less harmful to skin and eyes and is not flammable. The efficiency of ECL excitation with TPB is comparable to that with tripropylamine.

Obtained results indicate that potential at which the ECL emission raise is observed and ECL intensity are dependent on the film thickness, type and concentration of luminophor within the film as well as the potential scan rate. All mentioned parameters determine the kinetics and mechanisms of charge transfer processes within the films. We believe that such study allows obtaining new valuable data for designing different devices of organic optoelectronics including light emitting diodes, solar cells and sensors.

The work was supported by Science and Technology Center in Ukraine projects ##4495 and 5067 (Project manager Prof. Mykola Rozhitskii).

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Note OC-17 :

OC-18

SHAPE-CONTROLLED ELECTRODEPOSITION OF METAL NANOSTRUCTURES TROUGH USING SELF ASSEMBLED FONCTIONALIZED GOLD NANOPARTICLE TEMPLATE

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One of the desired structural goals in materials science is to obtain textured film on a large scale of metallic particles of nanometre or micrometer size and unique morphology. This challenge is motivated by the dependence of material properties on their shape and size and also by their potential application in nanotechnology. Many different shapes of metallic nanoparticles have been reported in literature including dendrites [1], triangular [2], disks [3] etc … Among the chemical methods used to achieve such morphologies, electrochemical one has been proved to be efficient for controlling the morphology of deposited metallic material on conducting substrate. The effects of applied potential or current induced shape evolution of deposited material are well known [2]. In the case of surfactant assisted morphology control, the applied potential can strongly influence surfactant adsorption behaviour on different facets, and could then direct the growth of particles into various shapes by controlling the growth kinetics along different crystal faces [2]. However, to control the particle shape using capping surfactant is still a challenge due to lack of knowledge on what surfactant or combination of surfactant would generate the desired particle shape.

In this work, we report the first example of the evolution of silver particles morphologies synthesized by electrochemical deposition on modified HOPG substrate by self-assembled gold nanoparticle (Au NP)[4-6]. For a convenient potential, controlling only the temperature causes a change in the deposited silver morphology from dendrite to plate (Fig. 1A, 1B). We can obtain different average sizes of plate by varying the deposition time. We show that the surface mobility of thiolate covered Au NPs surfaces can be the cause of the temperature-induced morphology evolution of electrodeposited silver. The wetting properties of deposited silver film were studied and surprising hydrophobic behaviour was observed (Fig. 1C) [5-6].

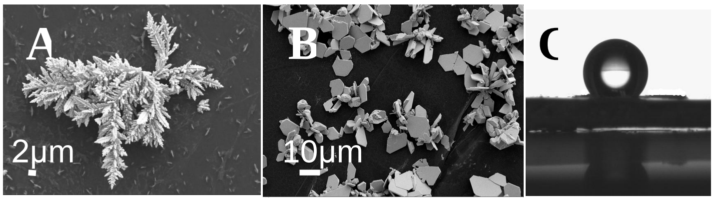

Figure 1.

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Note OC-18 :

RECENT ADVANCES IN THE PREPARATION AND ELECTROCHEMICAL USE OF ENSEMBLES OF NANOLECTRODES: FROM 2-D SURFACES TO 3D HIERARCHICAL NANOSTRUCTURES

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University Ca' Foscari of Venice (Italy)

Nanoelectrode ensembles (NEEs) are advanced electrode systems displaying interesting electrochemical characteristics useful for a variety of advanced applications, such as bio-electroanalytical devices, nanosensors and nanobatteries (1). NEEs are typically prepared by electroless or electrochemical deposition of metal nanoelements within the pores of a microporous templating membrane (2). The final geometry is a 2D surface composed by inlaid nanodisk electrodes embedded in the insulating membrane. 2D-NEEs present some unique characteristics such as highly improved signal/background current ratio, very low detection limits, high sensitivity to charge transfer kinetics (1); moreover, they are suitable to extreme miniaturization. However, 2D-NEEs show some limits in all those experimental situations where systems with high electroactive area are required, for instance, in the case of electrochemical devices and sensors based on the use of electroactive molecules or redox mediators immobilized on electrode surfaces. Recently, it was shown that 3D ensembles of metal nanowires can be obtained by plasma or chemical etching of 2D-NEE. Such 3D-NEEs have been successfully applied to prepare advanced electrochemical nanobiosensors (3,4), however, electrode systems with larger surface area and more controlled nano-geometries can further improve the electrochemical and sensing capabilities of these devices.

In the present communication two new different strategies to prepare 3D complex nanostructures on NEEs will be presented and discussed.

The first is based on the binding of gold nanoparticles on the surface of "conventional" 2D-NEEs; this is achieved by exploiting the binding properties of bifunctional thiols (5). The AuNPs are further functionalized with suitable thiolated biomolecules. In particular, we anchored thiolated single stranded oligonucleotide probes on the AuNPs. The hybridization with a complementary target was monitored using glucose oxidase as the enzyme label and a ferrocene derivative as suitable redox mediator. Experimental results obtained with this system constitute a proof of concept of feasibility of a rather complex NEE-based nano-architecture.

The second strategy brings to the preparation of ensembles of *metal nano-pine trees* (NPTs). In this case, the nanoarchitecture of each element is indeed composed by a metal *trunk* (corresponding to a nanowire of a 3D-NEE) on which *nanobranches* are grown by electrodeposition. Such NPT nanostructures are particularly attractive for gas-sensing and photoelectrochemical applications.

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Note OC-19 :

OC-20

DIRECT CONVERSION OF ENERGY BY CHEMICALLY POWERED MICRO-MOTORS

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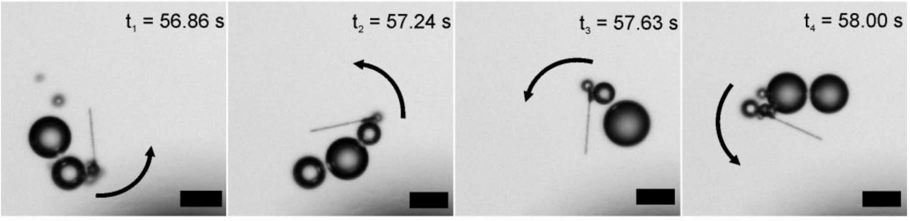
In the frame of the intensive development of smart micro/nanoscale objects, one fascinating field is dedicated to autonomous motors or swimmers, able to move in fluids under the influence of external parameters.[1] Generally there are three methods to induce the motion of these objects: Biochemical fueling which involves catalytically active enzymes, physical fueling by applying an external electric or magnetic field, and finally chemical fueling. In the latter case, the motion is generated by the direct conversion of locally available chemical energy into mechanical force promoted by catalysts that are selectively localized on organic/inorganic assemblies. In that context, most of the methods of preparation reported in the literature are based on non-trivial chemical engineering approaches which are time consuming, non-scalable and more importantly the localization of catalyst moieties are limited by poor spatial control.

In this contribution we have used carbon microtubes (CMTs) that are selectively modified in a dissymmetric way with a single-point metal electrodeposit.[2,3] The presence of a platinum cluster on the extremity of the tube allows the catalytic decomposition of hydrogen peroxide while the resulting oxygen bubbles trigger the controlled propulsion of the object.[4] Depending on the exact location of the catalyst moiety this allows the subsequent motion of these objects either on a linear or circular trajectory as exemplify by a 20 µm-long counter clockwise rotor.



Series of optical micrographs showing a micro-rotor. Scale bar: 10 µm.

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Note OC-20 :

OC-21

PHOTO-CATALYTIC BEHAVIOUR OF SELF-ORGANIZED TIO_2 NANOTUBES PREPARED IN ORGANIC ELECTROLYTES

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Preparation of the so-called third generation of self-organized TiO_2 nanotubes through anodization in organic electrolytes is receiving high attention due to the possibility to obtain longer and more regular structures.

Due to their useful semiconducting and photo-catalytic properties, these structures can be exploited in several technological fields as sensors, solar cell, membranes, photocatalysis.

Despite the huge number of studies available in literature, the complexity and the extent of the topic needs surely more investigation to understand correlations among morphology of these structures, their electronic properties and their working mechanism in presence of a light radiation.

This work wants to represent a contribution in deepening the insight in the field of application of these structures as anodes in the electrically enhanced water photo-splitting process for the production of hydrogen.

Some organic electrolyte containing fluorides have been chosen to carry out anodization of titanium sheets at different anodization times. After the annealing treatment, required to obtain crystalline structures, samples have been subjected to morphological, electrical and photo-electrochemical analysis.

A subsequent analysis on the correlation among the obtained data is proposed.

Note OC-21 :

GENETICALLY MODIFIED" SPIDER-LIKE OLIGOTHIOPHENES: ELECTRON PROPERTIES AND POLYMERIZATION ABILITY

Francesco Sannicolò[a], Tiziana Benincori[b], Simona Rizzo[c], Giovanni Rampinini[a],
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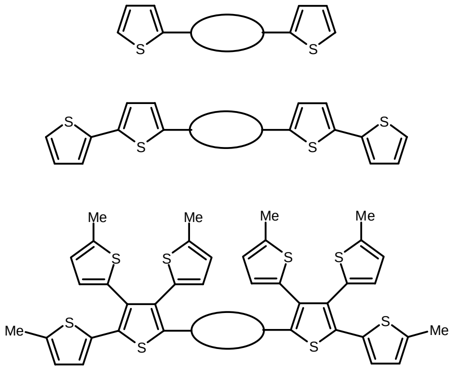
Multithiophene-based semiconductors are a well-known, popular class of organic semiconductors of very promising potential applications in a wide variety of fields, like electronics, energetics, sensoristics. Starting from our previous exhaustive work on "spider-like" branched oligothiophenes, affording a detailed and reliable rationalization of the relationships between structure and electronic properties[1,2], many structure modifications have been recently developed with respect to the original all-thiophene systems, aiming to achieve finer and wider modulation of both the HOMO and LUMO levels.



In particular, the "core" of our oligothiophene systems has been modified by choosing appropriate building blocks of different electron-richness, asymmetrically affecting both the LUMO and HOMO energy levels and localization along the main conjugated backbone, thus achieving one more freedom degree in tuning the electron properties of the molecule.

Our voltammetric investigation has been performed on a wide series of "genetically-modified" spider-like oligothiophenes, exploring both the effect of core modification at constant thiophene side chains, and the effect of increasing length and/or branching in the thiophene side chains at constant modified core. The core modification appears to be much more effective on the HOMO and LUMO energy levels and positions, while effective conjugation in the thiophene side chains is more determining on the oligomerization ability. The exhaustiveness of our investigation affords interpretative and predictive criteria which could usefully exploited in target-oriented molecular design.

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Benincori T., Bonometti V., De Angelis F., Falciola L., Muccini M., Mussini P.R., Pilati T., Rampinini G., Rizzo S., Toffanin S., Sannicolò F., *Chem. Eur.J.*, **2010**, 16, 9086

Note OC-22 :

WEDNESDAY 25 MAY

9:00 – 9:45 : IL4

Deronzier

Electrocatalytic Reduction at Nanostructured Materials: a Convenient Process to use CO_2 as a Renewable Carbon Source?

9:50 – 10:10 : OC 23

V. Jimenez

Electrochemical promotion phenomenon over carbon nanofiber catalyst-electrodes

10:10 – 10:30 : OC 24

J. Christophe

Electroreduction of carbon dioxide on copper-based electrodes : Activity of copper single crystals and copper-gold alloys

10:30 – 11:00

Coffee break

11:00 – 11:20 : OC 25

S. Rapino

Efficient water oxidation at carbon nanotube-polyoxometallate electrocatalytic interfaces

11:20 – 11:40 : OC 26

P. Kulesza

Enhancement of Pt-based catalysts towards oxidation of ethanol by supporting onto metal oxide matrices

11:40 – 12:00 : OC 27

W. Schuhmann

Noble-metal free catalysts for O_2 reduction and screening of materials libraries using electrochemical robotics

12:00 – 12:20: OC 28

S. Cassaignon

Controlled Synthesis by soft chemistry of Nano-textured Manganese Oxides for energy strorage.

ELECTROCATALYTIC REDUCTION AT NANOSTRUCTURED MATERIALS: A CONVENIENT PROCESS TO USE CO_2 AS A RENEWABLE CARBON SOURCE?

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Depletion and increasing costs of fossil resources have led to search for new alternative carbon raw materials for chemical synthesis. Utilizing renewable resources is a prerequisite for sustainable organic chemistry. One easily available green renewable carbon source is carbon dioxide (CO_2) which is naturally abundant, inexpensive, non-flammable and non toxic. The biggest obstacle in CO_2 utilization is its low energy level since CO_2 is the most oxidized form of carbon. Therefore the conversion of CO_2 requires the use of catalysts to overcome high kinetic barriers stabilizing CO_2. The catalytic electroreduction using molecular catalysts appears as a convenient method to achieve the transformation of CO_2 into more reactive forms such as HCOOH or CO.

In this context, we have developed a method to synthesize original electrocatalytic molecular redox systems, based on linear polymetallic chains involving non-bridged metal–metal bonds. An example of such molecular wire is $[Ru(bpy)(CO)_2]_n$ (bpy = 2,2'-bipyridine).

The metal–metal chain formation is easily achieved by electrochemical reduction of a mononuclear precursor complex like $[Ru(bpy)(CO)_2Cl_2]$ for instance, the resulting molecular wires being obtained as strongly adherent films on conducting surfaces. Those molecular cathodes operate at a low overpotential in pure aqueous electrolytes for the efficient electrocatalytic reduction of CO_2. The product selectivity toward CO/HCOOH can be tuned by varying substituents at the bpy ligands.

To facilitate the handling of this type of material in air and to avoid its disintegration, more practical materials have been also developed based on thin films of preformed polypyrrole (ppyr) N-functionalized by the precursor of those polymetallic chains.

Moreover in order to test the capabilities to this kind of material to reduce CO_2 into highly valuable compounds like fuels (hydrocarbons or alcohols) we have designed some new materials. We combined in a same polymeric matrix a metallic centre able to electroreduce CO_2 into CO with a catalytic one able to hydrogenate CO in-situ. Two strategies have been used, the first one involved a metallic complex known as an hydride producer, the second one platinum and non platinum metal nanoparticles

We will present here an account on the elaboration and characterizations of the whole kinds of polymetallic materials that we have developed and on their application as catalysts for electroreduction of CO_2. Some news orientations for the future will be also presented.

Note IL-4 :

ELECTROCHEMICAL PROMOTION PHENOMENON OVER CARBON NANOFIBER CATALYST-ELECTRODES

V. Jiménez[a], C. Jiménez- Borja[a], P. Sánchez[a], A. Romero[b], D. Theleritis[c],
E. I. Papaioannou[c], S. Brosda[c], S. Souentie[c], J. L. Valverde[a], C. G. Vayenas[c]

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A series of studies by Vannice in the 1980s reported on the high potential of iron complexes supported on graphitic carbon supports for Fischer-Tropsch synthesis [1]. Today well-defined and activated carbon nano-tubes (CNTs) and carbon nano-fibers (CNFs) are well established supports for a wide variety of applications such as Fischer-Tropsch synthesis, hydrogenation, and specifically, CO and/or CO_2 hydrogenation.

The effect of electrochemical promotion of Catalysis (EPOC) or non-Faradaic electrochemical activation of Catalysis (NEMCA) allows for the in situ control of the activity and selectivity of catalytic reactions taking place at the electrode-gas interface of solid electrolyte cells [1]. It has been shown by several surface science, catalytic and electrochemical techniques that the EPOC phenomenon (studied already for more than 70 catalytic systems, is due to the electrochemically controlled migration (spillover) of catalytically promoting anionic or cationic species (e.g. $O^{\delta-}$, $Na^{\delta+}$) from the solid electrolyte to the electrode-gas interface [2, 3].

In this study Ni and Ru impregnated carbon nanofibers have been for the first time successfully applied to a Y_2O_3-stabilized ZrO_2 (YSZ) solid electrolyte to form a catalyst-electrode cell. It has been demonstrated that CNFs or CNFs - YSZ composite electrodes are stable in oxidizing environment and at temperatures up to 450 ºC. These catalyst-electrodes exhibit satisfactory conductivity and porosity for electrochemical promotion studies.

The catalytic and electrocatalytic performance of this composite Ni or Ru CNFs have been investigated in the CO_2 hydrogenation reaction under atmospheric pressure and at temperatures from 200 to 450 ^oC. The only products observed were methane and CO under open circuit and electrochemical promotion conditions. Ni based catalyst-electrodes showed methane selectivity up to 55% at 300 ^oC, while the Ru based catalyst exhibited selectivity up to 75% at 390 ^oC. Both positive and negative applied potential enhances mildly the hydrogenation rate and the selectivity to CH_4 in the case of Ni catalyst-electrodes. Under negative applied potential, Ru based catalyst exhibit an enhanced hydrogenation rate with no further remarkable improvement of methane selectivity.

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Note OC-23 :

ELECTROREDUCTION OF CARBON DIOXIDE ON COPPER-BASED ELECTRODES : ACTIVITY OF COPPER SINGLE CRYSTALS AND COPPER-GOLD ALLOYS

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The electrochemical reduction of carbon dioxide has found its place in the environmental challenge as a way to recycle the gaseous CO_2. Among all the metals studied copper has revealed remarkable properties leading to the formation of hydrocarbons [1] whereas gold can reduce CO_2 to CO with the lowest overvoltage [2]. Many studies emphasize the importance of the surface state of the copper electrode for its activity towards the electroreduction of CO_2 [3,4].

In the present work we have first investigated the electrochemical reduction of CO_2 on well characterized Cu surfaces by cyclic voltammetry and electrolysis experiments. The use of single crystal electrodes allowed us to correlate the activity of the Cu electrodes to the atomic arrangement of the surface. The CH_4 formation is promoted on flat high density surfaces such as Cu (111) whereas CO is the major product on rougher surfaces.

In the second part of this work we have examined the activity of Au_xCu_y alloys. We have interpreted the voltammetric and electrolysis results as a function of the metal surface composition by considering the abilities of both metals for the reduction of CO_2. The CO production and the efficiency of the electrode increase with the gold contain in the alloy.

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Note OC-24 :

EFFICIENT WATER OXIDATION AT CARBON NANOTUBE-POLYOXOMETALLATE ELECTROCATALYTIC INTERFACES

Stefania Rapino[a], Matteo Iurlo[a], Massimo Marcaccio[a], Francesca Maria Toma[b], Andrea Sartorel[c], Francesco Paolucci[a], Marcella Bonchio[c] and Maurizio Prato[b].

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Water is the renewable, bulk chemical that nature uses to enable carbohydrate production from carbon dioxide. The dream goal of energy research is to transpose this incredibly efficient process and make an artificial device whereby the catalytic splitting of water is finalized to give a continuous production of oxygen and hydrogen. Success in this task would guarantee the generation of hydrogen as a carbon-free fuel to satisfy our energy demands at no environmental cost. Here we show that very efficient and stable nanostructured, oxygen-evolving anodes are obtained by the assembly of an oxygen-evolving polyoxometallate cluster (a totally inorganic ruthenium catalyst) with a conducting bed of multiwalled carbon nanotubes.

Our bioinspired electrode addresses one of the major challenges of artificial photosynthesis, namely efficient water oxidation, which brings us closer to being able to power the planet with carbon-free fuels.

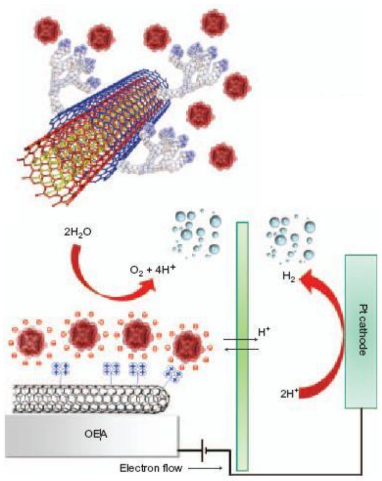

Fig.1 General scheme for a water-splitting electrocatalytic cell with the integrated nanostructured OEA.

Note OC-25 :

ENHANCEMENT OF PT-BASED CATALYSTS TOWARDS OXIDATION OF ETHANOL BY SUPPORTING ONTO METAL OXIDE MATRICES

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Platinum and platinum-based systems are so far the most active and practical electrocatalysts for low-temperature oxidation of organic fuels (formic acid, methanol, ethanol) in acid media. To enhance reactivity of Pt-based electrocatalysts can be achieved through the formation of bi- and trimetallic alloys such as Pt-Ru (oxidation of methanol), Pt-Pd (oxidation of formic acid), and Pt-Sn (oxidation of ethanol). Efficient electrocatalytic systems may also utilize robust large surface-area metal oxides which are capable of not only separating physically metal particles but also interacting with them thus affecting their chemisorptive and catalytic properties. The ideal matrix for electrocatalysis should be active either towards the inert reactant or the reaction intermediate. For example, tungsten oxide was demonstrated to activate Pt nanoparticles via specific electronic interactions in addition to hydrogen spillover and formation of highly conductive tungsten oxide bronzes. Improved fuel cell performances were found following addition of titanium, tungsten or niobium oxides due to the increase of the electrochemical active surfaces.

During oxidation of ethanol, a remarkable increase of electrocatalytic currents has been observed after modification of Pt-Sn nanoparticles with polyoxometallates of molybdenum or tungsten.. The presence of metal oxo species in the vicinity of platinum may result in mutual interactions and lead to changes in electronic structure of platinum and thus weaken the adsorption force towards bonding of poisoning carbon monoxide. We demonstrate here that efficient electrocatalytic systems can also be obtained with use utilizing zirconium oxide- supported Pt-Ru nanoparticles or even bare Pt reactive sites. The presence of ZrO_2 in the vicinity of Pt-Ru or Pt-Ru/C nanoparticles leads to the sizeable increase of their electrocatalytic properties in terms of the increase of the respective voltammetric and amperometric catalytic currents. Zirconium oxide may provide reactive centers itself or it may also influence catalytic activity of Pt-based metal nanoparticles. A possible explanation takes into account participation of ZrO_2 in the bifunctional mechanism that may be operative during electrooxidaion of ethanol. First zirconium oxide could be electrocative itself and may act as mediator of electron transfers, as well as it may provide, or stabilize interfacial Ru-oxo groups, and thus participates in removing the poisoning species (e.g. CO) from platinum surface. Zirconia can also serve as a good matrix for the third metal, e.g. rhodium or iridium; under certain conditions, its presence has a tremendous effect on the overall mechanism of the ethanol electrooxidation.

Note OC-26 :

OC-27

NOBLE-METAL FREE CATALYSTS FOR O_2 REDUCTION AND SCREENING OF MATERIALS LIBRARIES USING ELECTROCHEMICAL ROBOTICS

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The search for highly efficient catalysts to improve the efficiency of chemical conversions is an infinite pursuit. For many processes, the ultimate goal is to shift from the use of expensive and scarce catalysts to equally active or even superior catalysts which can be obtained cheaply from sustainable sources. For example, in fuel cell research, the quest to substitute prized catalysts based on platinum and other precious metals with non-precious metal based catalysts, or completely metal-free based catalysts for the reduction of oxygen is immense. Additionally, the necessary energy for driving such reactions or for production of suitable fuels may be harvested from the solar energy flux. To achieve this, photoelectro-catalyts have to be found which are suitable for making use of the solar energy flux. Thus, the goals of the meeting are addressed by discussing two topics related to the contribution of electrochemistry in nanostructuration of substrates for energy, namely on the one hand the search for noble-metal free electrocatalysts for O_2 reduction and on the second hand the search for photoelectrocatalysts for O_2/H_2 generation.

Several strategies in searching for novel noble-metal free electrocatalysts will be presented: *i)* the synthesis of modified carbon nanotubes and their properties as oxygen reduction catalyst in alkaline solutions, *ii)* the electropolymerization of metalloporphyrins to form thin films supported on carbon nanotubes and the subsequent pyrolysis of the obtained metalloporphyrin films under exclusion of oxygen, and *iii)* pyrolysis of N-containing polymers supported on carbon nanoparticles or carbon nanotubes.

For screening of photoelectrocatalysts a scanning droplet cell with integrated light fiber was developed which can be used to automatically record potentiodynamic photocurrent values as well as photocurrent spectra of small material spots selected by the droplet cell from a large materials library. The system set-up and first results concerning the investigation of semiconductor-based photoelectrocatalysts will be presented.

Note OC-27 :

CONTROLLED SYNTHESIS BY SOFT CHEMISTRY OF NANO-TEXTURED MANGANESE OXIDES FOR ENERGY STRORAGE.

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During the last years, research on lithium batteries has evolved toward nanoscaled electrode materials [1]. Among them different oxides were reported to present new reactinities and/or improved electrochemical behavior upon Li reaction in terms of rate capabilities [2] and reversibility [2-4] when the surface area is high and the crystallite size is sufficiently decreased.

Within this context, manganese oxide nanomaterials are of particular interest from a fundamental point of view to investigate structure and size effect on the electrochemical behavior owing to the richness of this family [5]. Nevertheless, tailoring the electrode materials structure/texture remains a significant challenge [6,7]. Our group develops the synthesis of manganese oxide nanoparticles by precipitation in aqueous medium at low temperature. This soft chemistry route is well known to provide a versatile control of the solid formation [8-12].

This presentation is focused on a low temperature aqueous route for precipitation of Mn(IV), Mn(III) or mixed valence Mn(III)-Mn(IV) manganese (oxyhydr)oxides using MnO_4^- and/or Mn^{2+} precursors. Soft conditions permit fine tuning of the reaction path and different pure phases are obtained depending on the synthesis conditions (*i.e.* acidity, oxidation state, temperature and aging). In particular, nanowires of cryptomelane $K_{0.11}MnO_{1.85}.(H_2O)_{0.75}$, manganite γ-MnOOH and pyrolusite β-MnO_2 are formed through self-assembly or topotactic processes, while γ-MnO_2 hollow nanocones originate from heterogeneous oriented attachment. In parallel, heterogeneous nucleation or heteroepitaxy can be controlled in order to obtain hierarchical nanoheterostructures such as core-corona architectures of lamellar birnessite $K_{0.19}MnO_{1,77}(H_2O)_{0.30}$ or cryptomelane-birnessite nanocomposites. Soft chemistry is therefore a valuable tool to investigate and to control nucleation-growth processes, as well as the resulting morphological characteristics. Using these well defined structures, shapes, sizes and hierarchical orders, some effects of the nanoscale on the electrochemical properties versus lithium are emphasized.

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Note OC-28 :

WEDNESDAY 25 MAY

14:00 - 14:20: OC 29

R. McCreery

Bridging the Gap between Single Molecule and “Large Area” Molecular Electronic Junctions

14:00 - 14:40: OC 30

M. Janin

Molecular Junctions Fabricated by Scanning Electrochemical Microscopy SECM.

14:50 - 15:10: OC 31

E. Maisonhaute

Do molecular conductances correlate with electrochemical rate constants? Experimental insights

15:10 – 15:30: OC 32

M. Hromadova

Facile electron transfer in molecular wires based on the extended viologens.

15:30 – 15:50:
Coffee break

Poster Session 1

OC-29

BRIDGING THE GAP BETWEEN SINGLE MOLECULE AND "LARGE AREA" MOLECULAR ELECTRONIC JUNCTIONS

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Haijun Yan, Stan Stoyanov, Andriy Kovalenko

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**Ohio State University, Columbus, Ohio*

We make "molecular junctions" consisting of aromatic molecules covalently bonded to disordered graphitic carbon substrates and completed with a Cu or Au "top contact". The phenyl-phenyl bond present between the molecular layer and the substrate result in strong electronic coupling and good thermal stability [1-3]. Microfabricated molecular junctions range from 2.5 x 2.5 to 400 x 400 um in area, and can withstand temperature excursions from 5 K to >450K without change in electronic behavior [4]. Current voltage cycles are reproducible from sample to sample, yield is 90 – 100 %, and the devices may be voltammetrically scanned at least 10^9 cycles without observable changes in electronic behavior. The electronic characteristics of the junctions depend strongly on the structure and thickness of the molecular layer, but are weakly dependent on temperature [1,2]. A new technique based on diffusion of metal atoms onto a molecular layer permits observation of the conductance of single molecules within a monolayer, and comparison to devices containing $>10^6$ molecules [5]. A detailed analysis of the conduction mechanism indicates that transport is consistent with tunneling of holes through the molecular HOMO, and governed by a modified Simmons relationship [1]. However, strong interactions between the molecules and the carbon substrate significantly perturb the energy levels of the molecules, and modify the tunneling barrier height. The results represent a significant step toward rational design of molecular electronic devices, and an understanding of the factors controlling electron transport through molecules.

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Note OC-29 :

MOLECULAR JUNCTIONS FABRICATED BY SCANNING ELECTROCHEMICAL MICROSCOPY SECM.

Marion Janin, Jalal Ghilane, Pascal Martin, Hyacynthe Randriamahazaka,
Jean-Christophe Lacroix

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With the need of miniaturization in microelectronics, the interest for organic nanodevices has been growing over the past decades. Molecular junctions are increasingly developped and studied.
In this work we will present the fabrication of metal/polymer/oligomer/metal junctions between two electrodes (SECM tip/substrate) operating in a SECM configuration. A conducting polymer is electrochemically deposited on the UME until the very moment it reaches the substrate (*Sketch*).

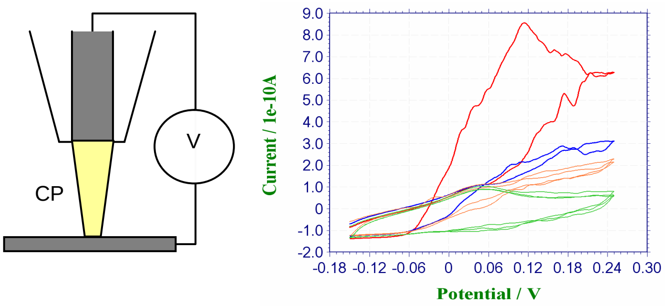

Figure: *Left*: SECM setup with CP deposited between two electrodes. *Right*: Conductance of the PANI nanojunction vs the applied potential. From top to bottom, the bias applied to the nanojunction is 6mV, 2mV, 1mV and 0mV. Scan rate 100mV/s

Using SECM setup doesn't necessitate the preliminary obtention of a nanometer gap between two electrodes; the initial system can be a micrometer gap, which requires a non-negligible amount of polymer to be deposited. Nevertheless, some of those junctions present very low conductance values which suggest that the electronic transport mechanism is controlled by a few oligomers only[1]. Unlike other techniques used to build molecular devices, the SECM enables the fabrication of reproducible and stable molecular junctions[2,3].
Depending on the redox state of those oligomers, the conductance of the organic junction varies from insulating to conductive (*Right figure*). This redox gated oligomer junction can thus play the role of a electrochemical transistor.

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Note OC-30 :

OC-31

DO MOLECULAR CONDUCTANCES CORRELATE WITH ELECTROCHEMICAL RATE CONSTANTS? EXPERIMENTAL INSIGHTS.

Emmanuel Maisonhaute,[a, b] Xiao-Shun Zhou[b, c, d], Ling Liu[d], Philippe Fortgang[b], Anne-Sophie Lefevre[b], Anna Serra-Muns[b], Nourredine Raouafi[e], Christian Amatore[b], Bing-Wei Mao[d], Bernd Schöllhorn[b, f].

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[b] UMR CNRS 8640 « PASTEUR », Ecole Normale Supérieure, , Université Pierre et Marie Curie-Paris 06, 24 rue Lhomond, 75231 Paris Cedex 05, France.
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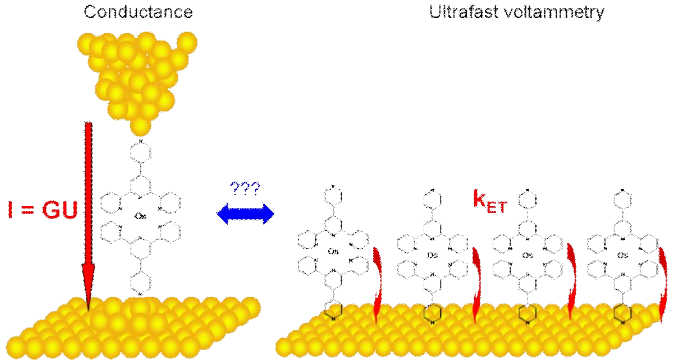
We measured single molecular conductance for three different redox systems self-assembled onto gold by the STMBJ method and compared them to electrochemical heterogeneous rate constants determined by ultrafast voltammetry. It was observed that fast systems indeed give higher conductance. Monotonous dependency of conductance on potential reveals that large molecular fluctuations prevent the molecular redox levels to lie between the Fermi levels of the electrodes in the nanogap configuration. Electronic coupling factors for both experimental approaches were therefore evaluated based on superexchange mechanism theory. This suggests that coupling is surprisingly on the same order of magnitude or even larger in conductance measurements whereas electron transfer occurs on larger distances than in transient electrochemistry.



References:

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Note OC-31 :

FACILE ELECTRON TRANSFER IN MOLECULAR WIRES BASED ON THE EXTENDED VIOLOGENS.

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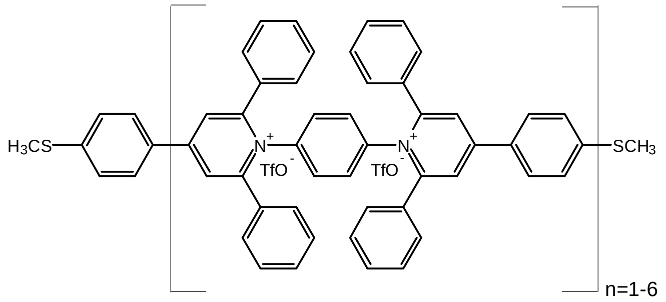
Facile electron transfer in molecules with one dimension greatly exceeding the other two is essential in the development of new molecular electronic devices. A series of molecules based on the extended viologens with n = 1 to 6 repeating units has been studied by electrochemical and spectroscopic methods. We show that the electron transfer in the shortest homologue of extended viologens (Scheme 1) with n = 1 is due to reduction of two identical communicating pyridinium moieties leading to a full charge delocalization, whereas the electron transfer in molecules with $n \geq 2$ is due to the reduction of initially non–communicating centers. This was also confirmed by digital simulation of the cyclic voltammograms.[1] The first standard redox potential of the molecules with $n \geq 2$ is constant and equal to E_{1m}^0 = -1.024 ± 0.001 V meaning equal probability of electron transfer into the individual redox moieties. Each molecule can accept reversibly four to ten electrons without any long term chemical changes. This was confirmed by the in–situ UV–Vis spectroelectrochemical detection. A possibility to repeat electron transfer without compromising the chemical stability and integrity of the molecule should be a prerequisite for its use in the field of molecular electronics. These studies were complemented by the measurements of the conductivities of individual metal–molecule–metal junctions using Tao's approach and the gold electrode substrate.[2] Original wires were chemically modified prior to the conductivity measurements leading eventually to dithiols, which were then chemisorbed onto the gold substrate. Current–distance curves were measured by scanning tunneling spectroscopy technique and the conductance histograms have been constructed. The single molecule conductance values decay exponentially with increasing length of the molecular wires and change from 5.1 nS to 3.1 nS for this series of molecules. Interestingly, the attenuation parameter β for these compounds is much smaller than for any other σ and π-conjugated systems known to us.



Scheme 1

A Grant Agency of the Academy of Sciences of the Czech Republic (IAA400400802), Grant Agency of the Czech Republic (GACR 203/08/1157, 203/09/0705) and Ministry of Education (MEB041006) are greatly acknowledged for the financial support.

References:

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Note OC-32 :

THURSDAY 26 MAY

9:00 – 9:45 : IL5

S. Palacin

Functional catalysts for hydrogen production and uptake, and oxygen reduction based on modified carbon nanotubes networks

9:50 – 10:10 : OC 33

Bonnefont

Oxygen Reduction Reaction on 3D Electrodes based on Vertically Aligned Carbon Nano-filaments

10:10 – 10:30 : OC 34

Zigah

Quantification of photoelectrogenerated hydroxyl radical on TiO_2 by surface interrogation scanning electrochemical microscopy (SI-SECM)

10:30 – 11:00

Coffee break

Poster Session 2

FUNCTIONAL CATALYSTS FOR HYDROGEN PRODUCTION AND UPTAKE, AND OXYGEN REDUCTION BASED ON MODIFIED CARBON NANOTUBES NETWORKS

Le Goff, A.[1]; Artero, V.[2]; Jousselme, B.[1]; Morozan, A.[1] ; Dinh, P. T.[2]; Guillet, N.[3]; Métayé, R.[1]; Fihri, A.[2]; Palacin, S.[1]; Fontecave, M[2]

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Interconversion of water and hydrogen in unitized regenerative fuel cells is a promising energy storage framework for smoothing out the temporal fluctuations of solar and wind power.

However, replacing currently used platinum catalysts by lower-cost and more abundant materials is a pre-requisite for this technology to become economically viable.

We recently showed that the covalent grafting of a nickel bisdiphosphine–based mimic of the active site of hydrogenase enzymes onto multiwalled carbon nanotubes results in a high–surface area cathode material with high catalytic activity, even under the strongly acidic conditions required in classical proton exchange membranes. Hydrogen evolves from aqueous sulfuric acid solution with very low overvoltages (20 millivolts), and the catalyst exhibits exceptional stability (more than 100,000 turnovers).

The same catalyst is also very efficient for hydrogen oxidation in this environment, exhibiting current densities similar to those observed for hydrogenase-based materials

Besides, similar carbon nanotubes networks are used as host matrix for various metallo-organic catalysts able to reduce oxygen.

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Note IL-5 :

OC-33

OXYGEN REDUCTION REACTION ON 3D ELECTRODES BASED ON VERTICALLY ALIGNED CARBON NANO-FILAMENTS

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The oxygen reduction reaction (ORR) is the reaction occurring at the cathode of polymer electrolyte fuel cells which are considered the power sources of tomorrow. In this work, we will present combined experimental and modeling study of the ORR on three dimensionally (3D) ordered catalytic layers composed of Pt nanoparticles supported on vertically aligned carbon nanofilaments (VACNF). The preparation method of these catalytic layers allows varying the layer thickness and the Pt coverage independently in a wide range of parameters (1,2). The experimental data were obtained by using rotating ring disc electrode (RRDE), while the simulations were performed using finite element approach (3). The mathematical modeling takes into account the spatial distribution of the Pt active sites, the mass transport of O_2 and H_2O_2 in the 3D VACNF architecture and realistic values for the reaction rates of the different ORR steps. Due to the high degree of homogeneity and structural order of the Pt/VACNF catalytic layers, the experimental current potential curves can be quantitatively compared to the simulated ones. The data obtained were interpreted within a dual path mechanism which comprises a series pathway involving H_2O_2 as intermediate species and a direct pathway occurring through the direct dissociation of O_2 (3).

In this presentation, special attention will be paid on the influence of the 3D structure of the catalytic layer on the kinetics of the ORR. In particular, the validity of the Koutecky-Levich analysis for the determination of the kinetics parameters of the ORR will be discussed with the help of experimental and simulated RRDE curves. Finally, the optimum 3D electrode structure for the ORR, leading simultaneously to a high Pt utilization factor with a low H_2O_2 production will be discussed.

Acknowledgement:
Financial support from ANR under the project ANR-06-CEXC-004 and European Commission under the project DEMMEA (Project Number 245156) is highly appreciated.

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Note OC-33 :

ElecNano^4- 7th ECHEMS
23-26 may 2011
Paris, France

OC-34

QUANTIFICATION OF PHOTOELECTROGENERATED HYDROXYL RADICAL ON TiO_2 BY SURFACE INTERROGATION SCANNING ELECTROCHEMICAL MICROSCOPY (SI-SECM)

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TiO_2 is a good semiconductor photocatalyst because of its large band gap (~3.1 eV) that prevents recombination of the photogenerated electron-hole pair. It is widely used as the anode in water splitting electrolysis cells to produce O_2 [1], as well as in the photodegradation of organic pollutants [2]. These photoinduced reactions are thought to proceed through the same $\cdot OH_{(ads)}$ intermediate.

The surface interrogation mode of scanning electrochemical microscopy (SI-SECM) [3] was used for the detection and quantification of adsorbed hydroxyl radical $\cdot OH_{(ads)}$ generated photoelectrochemically at the surface of a nanostructured TiO_2 substrate electrode. In this transient technique, an SECM tip is used to generate *in-situ* a titrant from a reversible redox pair that reacts with the adsorbed species at the substrate and produces a feedback signal from which the amount of adsorbate and its decay kinetics can be obtained.

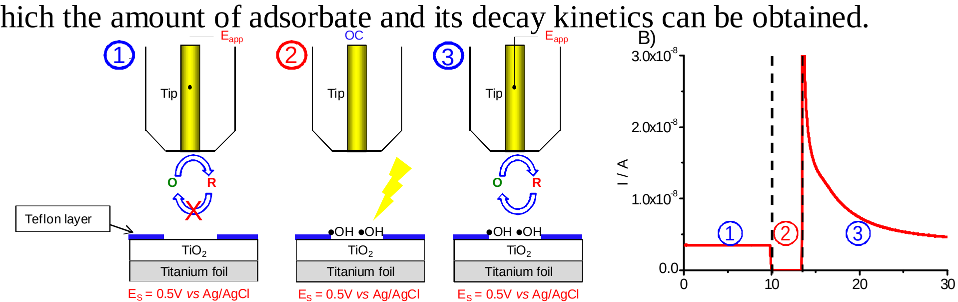


Figure 1*: A) Description of the surface interrogation technique for the reduction of $\cdot OH_{(ads)}$ on TiO_2. 1) No $\cdot OH_{(ads)}$ on TiO_2, the reduce species generate at the tip can no react with the surface. 2) Tip is open circuit, the light is on, $\cdot OH_{(ads)}$ are generate on TiO_2 by the hole generate by the surface irradiation. 3) Light is off, interrogation of $\cdot OH_{(ads)}$ by reduce species generate at the tip. B) tip current in function of time during the three steps describe on A), 1) Negative feedback current. 2) No current, tip is open circuit. 3) Interrogation current.*

A typical $\cdot OH_{(ads)}$ saturation coverage of 222 μC/cm^2 was found by its reduction with electrogenerated $Ir(Cl_6)^{3-}$. The decay kinetics of $\cdot OH_{(ads)}$ by reaction with itself to produce H_2O_2 was studied through the time dependence of the SI-SECM signal. The self-association constant and a diffusion coefficient for the adsorbed species were found by a fitting of the SI-SECM transients through digital simulations using commercial software. The use of a radical scavenger such as methanol competitively consumes $\cdot OH_{(ads)}$ and yields a shorter SI-SECM transient, where a pseudo-first order rate was determined.

References:

[1] Fujishima, A.; Honda, K., Nature, **1972**, *238*, 37.
[2] Mills, A.; Davies, R.H.; Worsley, D., Chem. Soc. Rev., **1993**, *22*, 417.
[3] Rodríguez-López, J.; Alpuche-Aviles, M. A.; Bard, A. J., J. Am. Chem. Soc. ***2008****, 130, 16985*

Note OC-34 :

THURSDAY 26 MAY

14:00 - 14:45: IL6

R. Crooks

Core-Shell Dendrimer-Encapsulated Nanoparticles: Theory, Synthesis, Characterization, and Electrocatalysis

14:50 - 15:10: OC 35

G. Loget

Synthesis of Janus type micro- and nanoobjects in the bulk phase by bipolar electrochemistry

15:10 – 15:30: OC 36

J. Ustarroz

New experimental approaches for the study of electrochemical nucleation and growth of nanoparticles: electrodeposition on TEM grids and in-situ SAXS investigation

15:30 – 15:50: OC 37

F. Mirkhalaf

Electrocatalytic Properties of Novel Bimetallic Au-Pt Nanoparticles as Reducing Substrates

15:50 – 16:30

Coffee break

16:30 – 16:50 : OC 38

V. Artero

H_2 electro-evolution catalyzed by cobalt-oxide nanoparticles and their oxidative transformation into an O_2-evolving catalytic film

16:50 – 17:10 : OC 39

Visy

Conducting polymer based magnetic nanohybrids in potential solar or fuel cell applications

17:10 – 17:30 : OC 40

Merki

Amorphous Molybdenum Sulfide as Catalyst for Electrochemical Hydrogen Production in Water

END OF THE MEETING

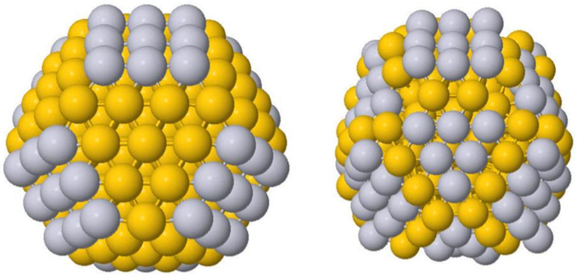
IL-6

CORE-SHELL DENDRIMER-ENCAPSULATED NANOPARTICLES: THEORY, SYNTHESIS, CHARACTERIZATION, AND ELECTROCATALYSIS

Richard M. Crooks, Emily V. Carino, Graeme Henkelman, Hyun-You Kim,
David F. Yancey, and Liang Zhang
Department of Chemistry and Biochemistry, The University of Texas at Austin
1 University Station, A5300, Austin, TX 78712-0165 USA

One approach for designing improved nanoparticle electrocatalysts involves the use of first-principles calculations, such as density functional theory (DFT), to predict the structural properties of efficient, new materials. As these types of calculations have begun to emerge, however, it has become increasingly clear that there are few or no experimental models available to test them. Dendrimer-encapsulated nanoparticles (DENs)[1] provide an opportunity to meet this need, because their size, composition, and structure can be controlled and because they have a size that is compatible with DFT calculations (< 100 atoms). DENs are synthesized by complexing metal ions with interior tertiary amines of poly(amidoamine) (PAMAM) dendrimers, followed by chemical reduction. By controlling the metal-ion-to-dendrimer ratio, the size of DENs can be controlled. In addition, bimetallic DENs have been prepared by complexing and chemically reducing different metals either simultaneously, which usually yields alloys, or sequentially, which can lead to core/shell structures. This chemical reduction method has proven effective, but here we will present a new approach for synthesizing core-shell DENs, which is based on the electrochemical method of underpotential deposition (UPD), that provides a means for exerting a higher level of control over shell structure.

Cu UPD onto Au[2] or Pt[3] DENs, having sizes ranging from 1.2 to 2.0 nm, results in core-shell nanoparticles. Our present understanding of both full- and partial-shell structures will be discussed from both experimental and theoretical perspectives. As illustrated schematically in the figure, both full and partial Cu shells on Au@Cu DENs can be replaced with Pt via a galvanic exchange reaction.[2] Both in-situ and ex-situ X-ray absorption spectroscopy (XAS) has been used to characterize these materials. More traditional characterization methods, such as cyclic voltammetry, UV-vis spectroscopy, and high-resolution electron microscopy also provide insights into the structure of these core@shell DENs. The electrocatalytic properties of these materials for the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) will be discussed as a function of the identity of the core metal and the identity and coverage of the shell. These experimental results will be correlated to preliminary DFT calculations.



References:

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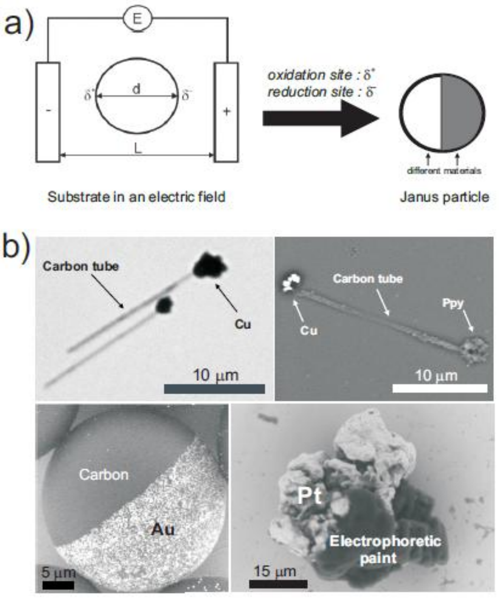
Note IL-6 :

SYNTHESIS OF JANUS TYPE MICRO- AND NANOOBJECTS IN THE BULK PHASE BY BIPOLAR ELECTROCHEMISTRY

Gabriel Loget, Zahra Fattah, Dodzi Zigah, Laurent Bouffier and Alexander Kuhn
Institut des Sciences Moléculaires, Université Bordeaux 1, ENSCBP, 16 Avenue Pey Berland, 33607 Pessac, France

Dissymmetric hybrid micro- or nanoobjets, so-called Janus particles, have a strong application potential in many areas ranging from molecular electronics to targeted drug delivery[1]. So far it has been quite difficult to achieve a dissymmetric modification at these scales and most approaches are based on using interfaces to break the symmetry. Only a few bulk procedures are known so far to produce these objects. In this context bipolar electrochemistry is a very appealing approach, which relies on the fact that when a conducting object is placed in a strong electric field a polarization occurs, that is proportional to the electric field and to the characteristic dimensions of the object. Therefore different redox reactions can be carried out simultaneously at the opposite ends of the object. This localized activity can be used for example to drive objects through a solution[2], but also for many other applications[3], including highly controlled electrodeposition.



a) Bipolar electrodeposition scheme. b) Examples of Janus particles obtained using bipolar electrodeposition.

Here we report several approaches, all based on bipolar electrochemistry, allowing us to synthesize a large variety of dissymmetric hybrid compounds with characteristic features in the micro- or nanometer range[4-7]. It is possible to modify either anisotropic or isotropic objects and to deposit metals, semiconductors and insulators with a high spatial control. Due to its versatility and because these modifications are carried out in the bulk phase, this process might become a major technology for the production of Janus particles, also at an industrial scale[8].

References:

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(2) Loget, G.; Kuhn, A. *J. Am. Chem. Soc.* **2010**, *132*, 15818.
(3) Mavré, F. *Anal. Chem.* **2010**, *82*, 8766.
(4) Warakulwit, C.; Nguyen, T.; Majimel, J.; Delville, M.-H.; Lapeyre, V.; Garrigue, P.; Ravaine, V.; Limtrakul, J.; Kuhn, A. *Nano Lett.* **2008**, *8*, 500.
(5) Loget, G.; Lapeyre, V.; Garrigue, P.; Warakulwit, C.; Limtrakul, J.; Delville, M.-H.; Kuhn, A. **2011**, *submitted*.
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(7) Fattah, Z.; Loget, G.; Warakulwit, C.; Limtrakul, J.; Bouffier, L.; Kuhn, A. *Electrochim. Acta* **2011**, in press doi:10.1016/j.electacta.2011.01.048.
(8) Kuhn, A.; Loget, G. French patent **2010**, N^o 1061031.

Note OC-35 :

NEW EXPERIMENTAL APPROACHES FOR THE STUDY OF ELECTROCHEMICAL NUCLEATION AND GROWTH OF NANOPARTICLES: ELECTRODEPOSITION ON TEM GRIDS AND IN-SITU SAXS INVESTIGATION

Jon Ustarroz,[a] Xiaoxing Ke,[b] Joshua Hammons,[c] Trevor Rayment,[c,d] Sara Bals,[b] Annick Hubin,[a] and Herman Terryn[a]

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[b] *EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium*
[c] *School of Chemistry, University of Birmingham, B15 2TT, Birmingham, U.K.*
[d] *Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus,Didcot, Oxfordshire OX11 0DE, U.K.*

Supported nanoparticles are important for many applications including electrocatalysis and electroanalysis. Although nanoparticles can be synthesized by a multitude of methods in solution or in gas phase, when it is required that the particles are firmly attached to a surface, previous methods may not provide the best solution. Recently, electrochemical deposition has arisen as an alternative for the nanostructuring of electrodes because of its ease of implementation and cost effectiveness.

Several groups have electrodeposited nanoparticles on various substrates but obtaining narrow size distributions is still a challenge. To overcome this problem, the early stages of electrochemical nucleation and growth should be completely understood. Such studies have been conventionally addressed by combining electrochemical characterization with ex-situ FESEM or AFM/STM characterization. However none of these techniques is suitable for high-resolution structural analysis of small nanoparticles. On the other hand, an ex-situ approach is always highly time-consuming as many samples are needed to study the kinetics of the reaction.

In this presentation we show two different innovative approaches to solve these problems and gain new insights in electrochemical early nucleation and growth phenomena.

First, the use of carbon coated TEM grids as electrochemical electrodes has been proven effective as electrochemical information on nucleation and growth, FESEM, HAADF-STEM, EELS and HRTEM data from the as-electrodeposited particles can be acquired from the same sample without the need of removing the particles from the substrate[1]. Results obtained by means of this approach underscore the importance of considering that an electrochemical aggregative growth mechanism may be involved in the early stages of electrochemical nanoparticle formation.

Second, the use of a specifically designed flow cell has also been proven effective to carry out in-situ SAXS studies on electrochemical systems[2]. We show here how this approach can be implemented to monitor in-situ the evolution of nanoparticle size distributions in potentiostatic multipulse electrodeposition.

References:

(1) Ustarroz, J.; Gupta, U.; Hubin, A.; Bals, S.; Terryn, H. *Electrochemistry Communications* **2010**, *12*, 1706.
(2) Hammons, J.A.; Rayment, T.; Vandendael, I.; Blajiev, O.; Hubin, A.; Davenport A.J.; Raes, M.; Terryn, H. *Electrochemistry Communications* **2010**, *12*, 717.

Note OC-36 :

ELECTROCATALYTIC PROPERTIES OF NOVEL BIMETALLIC AU-PT NANOPARTICLES AS REDUCING SUBSTRATES

Fakhradin Mirkhalaf

Sonochemistry Centre, Coventry University, Coventry, CV1 5FB, UK

There are currently extensive research efforts for developing efficient and selective electrocatalysts for the reduction of oxygen due to their importance in fuel cells. Metal nanoparticles have been extensively employed as electrocatalysts due to their large surface to volume ratios and high catalytic activity. We have previously reported a new method for synthesis of metal nanoparticles stabilized by metal-carbon covalent bonding in a two-phase system.[1] These nanoparticles contain no electroactive capping ligand and are good candidates to be used as electrocatalysts. In addition, we have recently shown that by providing local hydrophobic environment via selecting suitable stabilizing ligand around these nanoparticles, the selectivity of oxygen reduction can be further controlled.[2] In this case; metal cores act as mediators for the electron transfer process. In the present work, the synthesis and electrocatalytic properties of new bimetallic Au-Pt nanoparticles covalently capped with 1,4 decylphenyl groups is reported. The electrocatalytic properties of these nanoparticles on the reduction of oxygen were compared with that of the corresponding Au and Pt nanoparticles capped with the same ligand. The Au-Pt bimetallic nanoparticles showed enhanced electrocatalytic properties on both oxygen reduction and hydrogen evolution reactions. These nanoparticles support oxygen reduction channel to the peroxide formation. Hydrogen evolution on these nanoparticles occurs both in acid and alkaline solutions at relatively low overpotentials which was not observed for the analogous Au and Pt nanoparticles. These nanoparticles can be used as electrocatalysts for the production of molecular hydrogen and hydrogen peroxide and in fuel cells. It is proposed that these nanoparticles are good candidates to be used as electrocatalysts for the reduction of carbon and nitrogen oxides.

References:

(1) Mirkhalaf, F.; Paprotny, J.; Schiffrin, D. J.; *J. Am. Chem. Soc.*, **2006**, *128*, 7400-7401.
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Note OC-37 :

OC-38

H_2 ELECTRO-EVOLUTION CATALYZED BY COBALT-OXIDE NANOPARTICLES AND THEIR OXIDATIVE TRANSFORMATION INTO AN O_2-EVOLVING CATALYTIC FILM

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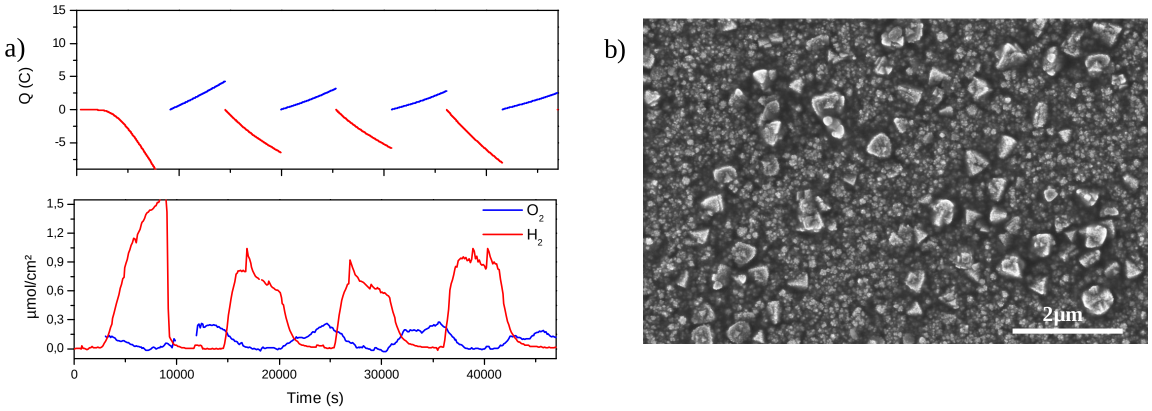
[b] *CEA, LITEN, Département des Technologies de l'Hydrogène, Laboratoire des Composants PEM (LCPEM), 17, Rue des Martyrs, 38054 Grenoble, France*
[c] *Collège de France, 11 place Marcelin-Berthelot, 75231 Paris cedex 05, France.,*

There has been a renewed interest in the past years for first-row transition metal oxide materials as catalysts for the oxidation of water and the evolution of O_2 under neutral pH 7 conditions.[1,2] Such catalysts, usually formed under oxidative conditions, thus hold promises for the substitution of noble metals (Pt, IrO_2) at the anode of water electrolysers. We also found that cobalt oxide materials can also be deposited onto FTO or carbon electrodes under reductive conditions, though as nanoparticles in this case, and that such particles catalyze H_2 evolution under neutral conditions. The structural characterization and electrocatalytic properties of these nanoparticles will be described. Actually, this material was found to be a bifunctional catalyst, also active for oxygen evolution, when the potential was switched to oxidative conditions. The catalytic switch is correlated with a reversible structural transformation of the cobalt deposit.



a) Charge passed through a FTO electrode (1 cm^2) during controlled potential coulometry initially at –1 V vs. Ag/AgCl in 0.5 M KPi, pH 7 electrolyte containing 0.5mM $Co(NO_3)_2$ and after transfer to a cobalt-free 0.5 M KPi, pH 7 electrolyte, with potential switching between oxidative (blue, 1.16 V vs. Ag/AgCl) and reductive conditions (red, –1 V vs. Ag/AgCl); Hydrogen and oxygen evolution detected by gas chromatography c) SEM images of the cobalt nanoparticles formed at the electrode under reductive conditions.

References:

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Note OC-38 :

CONDUCTING POLYMER BASED MAGNETIC NANOHYBRIDS IN POTENTIAL SOLAR OR FUEL CELL APPLICATIONS

Csaba Visy, Csaba Janáky, Balázs Endrődi

Department of Physical Chemistry & Materials Science

University of Szeged, Szeged, Hungary

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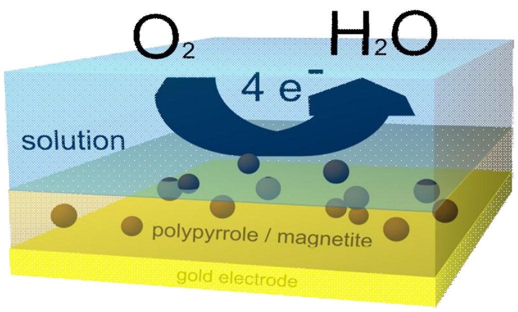
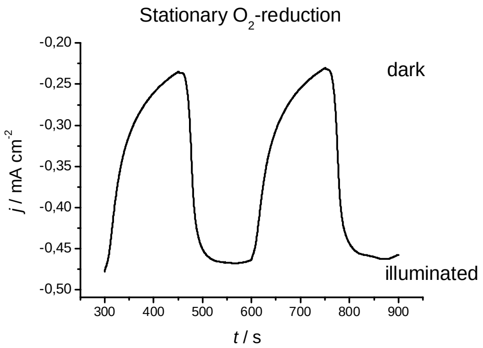
Conducting polymer based nanocomposites are more and more intensively studied since the end of the 1990's. These inorganic–organic hybrids form a promising class of new materials, owing to the advantageous properties of the polymer matrix and the embedded inorganic particles. The combinations often lead to synergistic effects, resulting enhanced properties, making these materials applicable in various fields.

Iron containing nanoparticles were incorporated into polypyrrole, polyaniline and PEDOT[1] through chemical and electrochemical synthetic procedures. Magnetite/Polypyrrole hybrid layers were electrochemically deposited on gold electrode by exploiting the chemical interaction between the nanoparticles and the conducting electrolyte (K-tetraoxalate). The prepared hybrid thin layers have proved to be photo-electro-catalytically active in the O_2 reduction reaction[2], so they can be exploited as cathode materials in fuel cells. The rate of the reduction could be doubled by illumination with white light, where the photocurrent was the consequence of the electrochemical decomposition of the intermediates, primarily the hydrogen-peroxide.





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Acknowledgment: Support through the project TÁMOP-4.2.1/B-09/1/KONV-2010-0005 is gratefully acknowledged.

Note OC-39 :

AMORPHOUS MOLYBDENUM SULFIDE AS CATALYST FOR ELECTROCHEMICAL HYDROGEN PRODUCTION IN WATER

Daniel Merki, Heron Vrubel, and Xile Hu

Ecole Polytechnique Fédérale de Lausanne, SB-ISIC-LSCI, BCH 3201, 1015 Lausanne, Switzerland

Amorphous molybdenum sulfide films are efficient hydrogen evolution catalysts in water. The films can be prepared via different electrochemical deposition methods. The method using consecutive cyclic voltammetry instead of a constant potential leads to the film with the highest and most stable catalytic activity. The film catalyzes proton reduction in a wide range of pHs and rather high geometric current densities are achieved at low overpotentials, e.g. up to 15 mA/cm^2 at $\eta = 200$ mV in 1 M H_2SO_4. The current efficiency for hydrogen production is quantitative. The molybdenum sulfide film can be doped with first-row transition metals by adding the respective metal ions to the deposition solution. The doped films show increased catalytic activity in terms of both, exchange current density and current densities at higher overpotentials.

Note OC-40 :

POSTERS SESSION

Wednesday 25 May, 15:30 – 19:00
Thursday 26 May, 10:30 – 12:30

PC-1

ELECTROCHEMICAL VERSUS PHOTOCHEMICAL GRAFTING OF ACETONITRILE ONTO METALS

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Jean Pinson[a] and Fetah I. Podvorica[a,b]

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[b] *Chemistry Department of Natural Sciences Faculty, University of Prishtina, rr. "Nëna Tereze" nr. 5, Prishtina, Kosovo.*

Nanometer thick organic films are obtained on copper, iron, nickel, gold and hydrogenated silicon surfaces by grafting acetonitrile (CH_3CN) via electrochemistry or photochemistry.
The electrochemical reduction of 2,6-dimethylbenzenediazonium tetrafluoroborate (2,6-DMBD) in ACN forms the 2,6-dimethyl phenyl radical, which cannot be grafted to the electrode surface due to steric hindrance[1]. However, this radical can abstract a hydrogen atom from acetonitrile (which is present in large concentration), thus forming the cyanomethyl radical, $^{\cdot}CH_2CN$, that binds to the metallic or semiconductor surface[2]. The same radical can be obtained by reduction of I, $BrCH_2CN$,[3] but also through UV irradiation of a thin film of ACN deposited onto the metal surface.[4]
In both cases, the composition and structure of the film are evidenced by IRRAS, Tof-SIMS and SEM and its thickness is measured by ellipsometry or optical profilometry. The structures are similar, as shown in Figure 1 for the IRRAS NH_2 deformation band at 1600 cm^{-1}. Under photochemical activation, the growth of the layer is due to the cyanomethyl radical while it is due to the cyanomethyl anion under electrochemical activation. Surface patterning of metal surfaces is presented as an application of the photochemical method.

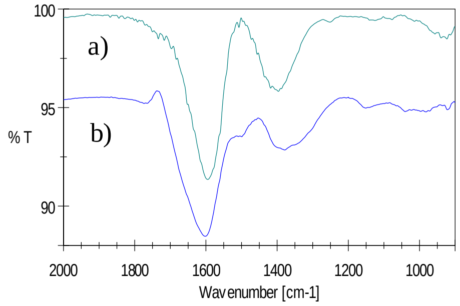

Fig. 1. IR spectra of a copper plate (NH_2 deformation band) grafted by ACN through: a) electrochemical reduction of 2,6-DMBD in acetonitrile (E= - 0.9 V/SCE) and b) 10 min UV irradiation of a thin layer of ACN deposited onto the copper plate.

References:
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MOLECULAR SEMICONDUCTORS – DOPED INSULATORS (MSDI) HETEROJUNCTIONS AS NEW CONDUCTIMETRIC DEVICES

M. Bouvet

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marcel.bouvet@u-bourgogne.fr

Whereas organic FETs and diodes have been prepared after their inorganic counterparts, we designed and characterized new molecular material based devices. Molecular Semiconductors – Doped Insulators (MSDI) Heterojunctions were built around an heterojunction between a molecular semiconductor (MS) and a doped-insulator (DI). MS must be more conductive than the sub-layer to take advantage of the heterojunction. Up to now, the lutetium *bis*phthalocyanine ($LuPc_2$) and lanthanide triple decker complexes have been used as MS. DI can be p-type materials, as non-substituted phthalocyanines (ex.: CuPc), or sexithiophenes, or n-type-materials, as fluorinated phthalocyanines (ex.: $Cu(F_{16}Pc)$) or perylene derivatives. MSDIs exhibit current-voltage characteristics shown below. The difference in the charge type of the two materials and in their density can affect the energy barrier at the interface leading to a variable extent of the plateau in the I(V) characteristics.
MSDIs have been used as new transducers for gas chemosensing. Thus, p-type materials (F0 in Fig.) lead to MSDIs that exhibit a positive response to ozone and a negative response to ammonia, whereas MSDIs prepared from n-type materials (F16 in Fig.) exhibit a positive response to ammonia and negative response to ozone. The remarkable point is that the only material in contact with the analytes is in all cases the same semiconductor.

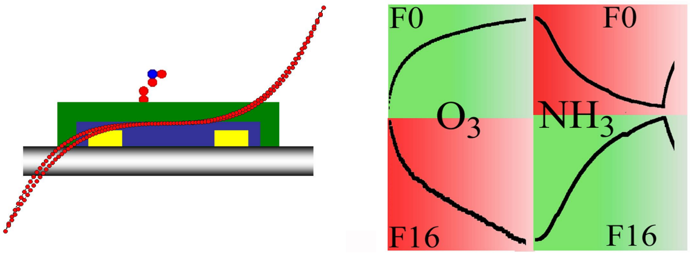

Figure:
left: scheme of a MSDI heterojunction, and a typical I(V) characteristics;
right: response of $LuPc_2$ / CuPc (F0) and $LuPc_2$ / $Cu(F_{16}Pc)$ (F16) MSDIs to O_3 and NH_3

References:

(1) Bouvet, M.; Pauly, A. in *The Encyclopedia of Sensors*, ed. by Grimes, C. A.; Dickey, E. C.; Pishko, M. V. American Scientific Publishers, **2006**, vol. 6, 227-270.
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(4) Chen, Y.; Bouvet, M.; Sizun, T.; Barochi, G.; Rossignol, J.; Lesniewska, E. *Sensors and Actuators B*, **2010**. DOI: 10.1016/j.snb.2010.11.042

PC-3

SCANNING ELECTROCHEMICAL MICROSCOPE AS AN ETCHING TOOL FOR A DIRECT ITO PATTERNING.

J. Charlier,[a] F. Grisotto,[a] R. Metaye,[a] B. Jousselme,[a] S. Palacin and B. Geffroy,[b]

[a] *CEA Saclay, IRAMIS, SPCSI, 91191 Gif sur Yvette Cedex, France*
[b] *CEA/Ecole Polytechnique, LPICM, 91128 Palaiseau, France*

Indium tin oxide (ITO) is a wide band gap n-type semiconductor, known for its good transparency and relatively high conductivity when deposited as a thin film on glass or flexible transparent substrates. Fine patterning of ITO films is a necessity for the development of new display technology that requires transparent and conductive electrodes, such as bioelectronic sensing, micro-nano structuration for optical devices, pixels for LED - OLED displays, organic solar cells… To optimize the performances of such devices, clean patterning technique i.e. straight sidewalls and respect of surface chemistry and physical properties is needed. The main drawbacks of the existing patterning techniques (i.e. lift-off and wet or dry etching) are the uncontrollable sidewall shape, the surface contamination with ITO residues, the damages to the substrate, especially for the flexible one. This leads to a global degradation of the electrical and optical properties. Moreover, most of these techniques require the use of strong acids (halogen acid, aqua regal) or toxic gases (for plasma treatment) and are usually multi steps and high cost processes.

We report here a simple and one step patterning technique of ITO using the scanning electrochemical microscopy as a soft etching tool. This direct lithographic technique provides a fast and low cost patterning process. Local etching of the ITO film is performed in aqueous acid electrolytic solution, in a SECM environment. This technique leads to a clean etching with straight walls (fig. 1) and no redeposition of the ablated part. The subjacent substrate (glass of polymer) is not damaged by this technique and the electrical and optical properties of the ITO film are preserved (fig. 2).

Fig. 1: AFM image of a straight etched line of ITO film using a 50-

Fig.2: OLED performed by localized ITO etching (black area) with SECM

References:

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USING A MEDIATING EFFECT IN THE ELECTROREDUCTION OF ARYLDIAZONIUM SALTS TO PREPARE THICK CONDUCTING ORGANIC FILMS

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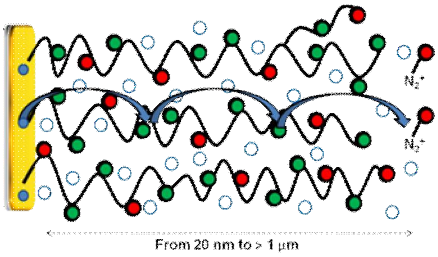
Extended cyclic voltammetric sweeping on aryldiazonium salts carrying an electroactive moiety (e.g., nitrobenzene, anthraquinone or benzophenone) allows the formation of thick conducting films, even in the micrometer size range, in a controlled manner in acetonitrile.[1] The method can successfully be carried out on various types of conducting materials such as carbon and metals. In many aspects, the electrochemical behavior resembles that of electroative polymers but with the important notion that the films produced herein are covalently attached at the surfaces. The growth mechanism involves two concomitant phenomena, i.e., continuous layer opening through desorption of physisorbed species and the mediating effect (Scheme 1).



Scheme 1. Proposed Model Describing the Film Growth during Potential Sweeping on Aryldiazonium Salts Carrying an Electroactive Moiety.

In this respect, the use of the sweeping technique is essential for the diazonium salts studied herein, noticing that the film growth comes to a halt already at a thickness of a few nanometers, if the surface film is created by way of potentiostatic electrolysis. The redox moieties are the central units in the transport of electrons from the surface to aryldiazonium molecules at the outer layer. In particular, surface-immobilized nitrophenyl groups are found to be efficient, because of the fact that they, upon reduction, are able to reduce the corresponding diazonium salt with a high rate while, at the same time, having the required chemical stability against being irreversibly protonated by the residual water in acetonitrile.

In future studies, it would be interesting to investigate the prospect of using these thick films, which exhibit large electrochemical signals, as sensors.

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ELECTROCHEMICAL MICROFLUIDIC PAPER-BASED ANALYTICAL DEVICES USING A GLUCOMETER FOR POINT-OF-CARE DETECTION OF MULTIPLE ANALYTES

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Electrochemical biosensors are capable of quantitative analysis with high sensitivity and are quite unaffected by use-environment. One of the most successful commercial systems is the glucometer (figure 1A). This portable electrochemical reader allows diabetes patients to self-monitor their glucose concentration in blood with a quick and easy test. The present work is part of a broad effort to develop high-quality, low-cost biomedical analysis in formats appropriate for use in the developing world and in other environment in which resources are limited.[1-3]

The system we developed consists of a microfluidic paper-based electrochemical device (EμPAD) used with a portable electrochemical reader (a glucometer) to detect various analyte (in addition to glucose), such as lactate, or cholesterol.[4] We took advantage of an already highly developed, commercial technology and adapted it for other applications and, the EμPADs acting as test strips, the cost significantly decreased.

The microfluidic channel of the EμPAD was realized by patterning paper with wax-printing technique already described,[5] then the electric circuit and electrodes were screen printed on top of it (figure 1B). We have demonstrated the use of these EμPADs with the True Track blood glucose meters to successfully detect and quantify analytes (glucose, lactate or cholesterol) thanks to enzymatic reactions and using potassium ferricyanide as a mediator. Aside from molecules of interest in blood analysis, we were also able to use this system to quantify ethanol in aqueous solutions.

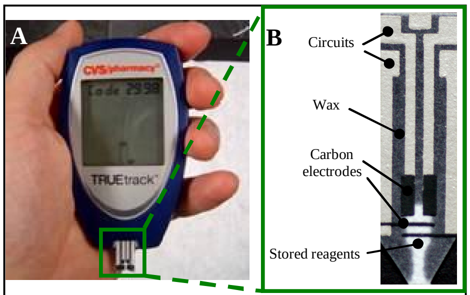

Figure 1: A glucometer in use with a EμPAD (A) Details of a EμPAD showing the zone where the reagents are stored and where the sample will be lead by the microfluidic channel patterned in the paper

This point-of-care electrochemical analytical system is capable of quantitative detection of a wide range of analytes with advantages such as i) simple, fast, portable, light weight and low-cost system, ii) no professional personnel needed, or iii) insensitive to light level, dust and insoluble particulates.

Electrochemical sensors like the present EμPADs associated with a simple reader are key systems to publicize electrochemical analysis as fast, reliable, easy-to-use, and low-cost for numerous applications.

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ON THE MECHANISM OF HYDROGEN EVOLUTION CATALYSIS BY PROTEINS. A CASE STUDY WITH BOVINE SERUM ALBUMIN

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The hydrogen evolution reaction (HER) and its reverse process the hydrogen oxidation reaction (HOR) have attracted for decades a huge attention from the electrochemical community. Not only is it an archetypal system to understand at the fundamental level the electrochemical reaction mechanisms, the catalytic and electrocatalytic processes or the influence of the electrode materials, but it is also of paramount importance for future application in fuel cell technologies or hydrogen production plants. A lot of work is thus aimed at improving the efficiency of the HER by electrocatalysis and bioelectrocatalysis. Although hydrogenases are, among proteins, the most obvious candidates for large scale hydrogen production, it is well established that many if not all proteins are able to catalyse the HER in certain conditions. Interestingly, it should be possible to use the catalytic HER to get information about protein structures, allowing the development of new electrochemical tools in proteomics. Such a goal requires a good understanding of the catalytic mechanism, which is currently lacking. In the present work, we investigate the catalytic properties of a protein, bovine serum albumin (BSA), at the hanging mercury drop electrode, and the results are analysed in the framework of a mediated electrochemical catalysis, based on the acid-base properties of the protein:

$$\begin{aligned} \mathrm{PH\ (ads)} + e^- &\leftrightarrows \mathrm{P^-\ (ads)} + \tfrac{1}{2}\,\mathrm{H_2} \\ \mathrm{P^-\ (ads)} + \mathrm{BH\ (aq)} &\leftrightarrows \mathrm{PH\ (ads)} + \mathrm{B^-\ (aq)} \end{aligned}$$

In this chemical catalytic mechanism (EC’), the electrolyte buffer (BH) acts as a proton donor for the HER, which is mediated by the adsorbed protein (PH). Within the framework of the above mechanism, a very good qualitative agreement is found between our experimental results and existing theories regarding the EC’ mechanism, although some differences are emphasised. It is shown that, under the experimental conditions, a "total catalysis" phenomenon occurs, where the rate is limited by the diffusion of the buffer proton donor. Besides, the buffer concentration dependence undoubtly points to slow electron transfer kinetics.

Using the proposed model, the catalytic efficiency can be assessed in terms of dimensionless kinetic parameters, and qualitative information can be gathered regarding the properties of the protein and the proton donor (rate constants, pK_a). Conversely, the potential efficiency of proteins for HER catalysis can be assessed from their known properties.

PC-7

THERMAL TREATED MANGANESE (III) TETRAPHENYLPORPHYRIN ACETATES/PLATINUM NANOPARTICLES SUPPORTED ON CARBON AS AN ELECTROCATALYST FOR OXYGEN REDUCTION

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Polymer electrolyte membrane fuel cells (PEMFCs) are efficient and clean electrochemical power generation devices that produce electricity from H_2 and O_2 gases. Platinum remains the catalyst of reference for the oxygen reduction reaction (ORR) in PEMFCs. Its high cost and poor availability makes the development of non-noble metal catalysts highly desirable.

Manganese (III) tetraphenylporphyrin acetates can chemically adsorbed on Pt/C under heat treatment condition in 400-600^{0}C. The morphology, distribution, and surface elemental analysis of the catalysts are characterized by X-ray diffraction spectroscopy and scaning electron microscopy and EDAX .Manganese (III) tetraphenylporphyrin acetate: Mn(TPP)OAc, Manganese (III) tetra-4-methoxyphenylporphyrin acetate: Mn(T4-OMePP)OAc, Manganese (III) tetra-4-nitrophenylporphyrin acetate: Mn(T4-ONO2PP)OAc can homogeneously anchor on the carbon support and withstand decomposition upon heat treatment at 600^{0}C. This new Catalysts are evaluated for electroreduction performances of oxygen on modified electrodes in sulfuric acid solutions. Manganese (III) tetraphenylporphyrins was dissolved in N,N-dimethylformamide (DMF) under stirring. Pt/C (20wt% Pt) was added to this solution and stirred at 60^{0}C for 24 h. Subsequently, the suspension was filtered and the precipitate was rinsed thoroughly with ethanol and deionized water. The residue was dried in vacuum at 90^{0}C for 12 h and then ground into fine powder. The resultant Mn(TPP)-Pt/C powder was subjected to heat-treatment in a quartz tube furnace at temperatures ranging from 300 to 600^{0}C under argon atmosphere The activity, stability, and selectivity of the catalyst presented in this paper are proven better than those of other common catalysts.

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THEORETICAL INVESTIGATION OF THE DISSOCIATION DYNAMICS OF ASYMMETRIC ALKYNYL(ARYL)IODONIUM RADICALS: CAN AB-INITIO DRC APPROACH PREDICT THE SELECTIVE WAY TO FUNCTIONALIZE SURFACES?

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The dissociation process of neutral open shell $[4\text{-F}-(C_6H_4)-I-C{\equiv}C-Cl(CH_2)_4]$ and $[4\text{-NO}_2-(C_6H_4)-I-C{\equiv}C-Cl(CH_2)_4]$ asymmetric iodonium radicals is theoretically studied. Vertical electron affinities and DRC (Dynamic Reaction Coordinate) results are obtained and compared with experimental evidences. In particular, the fluorine and nitro groups substituents are selected i) for their antitethic “electron withdrawing/electron donating” characteristics ii) the experimental evidence that the grafting ability, in terms of alkynyl/aryl grafting ratio, increases with the decreasing electron withdrawing nature of the substituent in the phenyl para position. DRC results show that the dissociation dynamics of the iodine–alkynyl carbon bond, for the nitro substituted iodonium, occurs on a longer time scale if compared to that one of the fluorine substituted iodonium. This finding is in agreement with the overall experimental outcome [1].

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ADSORPTION OF AMPHOLYTES AT ELECTRIFIED INTERFACES: THE ROLE OF ELECTROSTATIC INTERACTIONS AND INTERFACIAL CHARGE REGULATION

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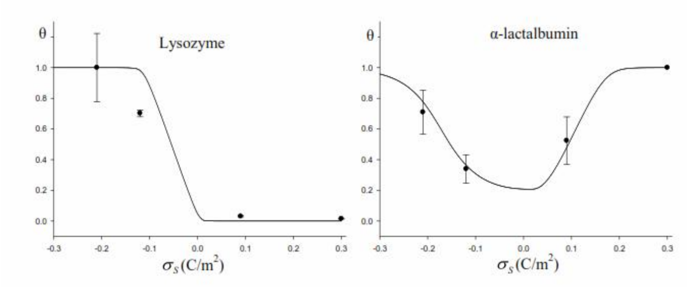
The adsorption of ampholytes such as proteins and peptides at charged surfaces is of importance in a wide range of scientific disciplines including surface engineering, heterogeneous biocatalysis, design of novel drug delivery systems for proteins and peptides and in separation sciences. The ionic environment close to a charged interface is different from that existing in bulk solution which may lead to charge regulation of an adsorbing ampholyte. The adsorbing ampholyte may also exert a charge regulating effect on the charged interface. The combination of these processes is termed *interfacial charge regulation*[1] and may be observed at any charged interface such as eg at nanoparticles, cell membranes, porous solid materials or electrified solid-liquid or liquid-liquid interfaces. In this work, electrochemistry at Interfaces between Immiscible Electrolyte Solutions (ITIES) is utilized to conduct a systematic experimental study on interfacial charge regulation of a series of model peptides and proteins. A theoretical model is developed which is effectively able to account for interfacial charge regulation of adsorbing ampholytes at ITIES. In a modified form the model may also be used to describe adsorption of ampholytes at solid interfaces as shown in the figure below.[2] The model can for example explain the counterintuitive observation that the overall negatively charged □-lactalbumin adsorbs at an overall negatively charged interface. The model can successfully account for the adsorption behavior of a series of model ampholytes measured by impedance based techniques at ITIES. These results are relevant for the understanding of protein adsorption in general and for quantifying the role of interfacial charge regulation.



Relative coverage, θ, as a function of surface charge, σ_s, for lysozyme (left) and α-lactalbumin (right) at pH 7.4.

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INTERVALENCE CHARGE TRANSFER (IV-CT) IN A MIXED VALENCE COMPOUND MODIFIED BY THE FORMATION OF A [3]-PSEUDOROTAXANE.

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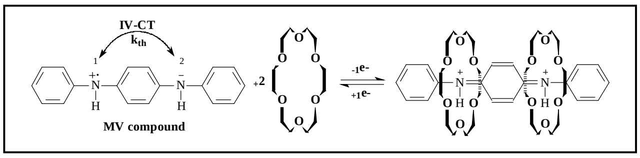
Electrochemical and spectroscopic properties of N,N-diphenyl-1,4-phenylenediamine (PDA), were investigated in the absence and in the presence of 18-crown-6-ether (CE), in tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$) solution in acetonitrile (ACN) with and without trifluoroacetic acid (TFA). In all solutions, PDA undergoes two reversible oxidation processes, corresponding to the radical cation considered as a mixed valence MV compound and to the dication. In neutral ACN, increase of CE induces a shift to lower potentials of the peaks of only the second redox process in comparison to the cyclic voltammograms obtained in CE free solution. This shift is attributed to the formation of a [3]-pseudorotaxane between PDA dication and 2 CE molecules (association constant K_a=7 10^7 M^{-1}). As a consequence, the intervalence charge transfer (IV-CT) rate constant between the two nitrogen atoms in the MV compound decreases from k_{th}= 1.35 $10^{10}s^{-1}$ for CE free solution to k_{th}=3.6 10^9s^{-1} in neutral ACN at [CE]/[PDA] = 20 and its comproportionation constant K_{co} decreases from 4.3 10^6 in CE free solution to 2.4 10^3 , at [CE]/[PDA] = 10. In TFA-ACN solution (+ 0.1 M $TBAPF_6$), and when the concentration of TFA is increased, both redox waves are shifted to more anodic potentials compared to their conterparts in neutral ACN. But, when [CE] is increased, both redox waves are shifted to negative potentials. This is attributed to the formation of host guest inclusion complexes of CE with each of PDA species. Consequently, the K_{co} deceases (4.3 10^4) when compared to that in neutral ACN; and the presence of CE does not change it; indicating no change in the lifetime of the MV compound. For IV-CT rate constant k_{th} in the MV compound, the presence of TFA decreases its value in CE free solution (1.4 10^9s^{-1}); whereas, the addition of CE in this medium increases the same IV-CT rate constant (k_{th}= 2.3 10^{10} s^{-1} for [CE]/[PDA] = 20). The interaction between CE and the PDA dication is confirmed by *in situ* UV-visible spectroscopy, which shows a red shift in λ_{max} of this species in the presence of CE when compared its λ_{max} in CE free solution in all media with or without TFA.



From these results, we show for the first time, the possible control of the IV-CT rate, through the lifetime and the potential domain of a MV compound prevalence. This control is not obtained as usual by chemical modification [1] of the structure of the starting molecule; but simply by varying either medium acidity and/or CE concentration as external stimuli, what leads to a reversible formation/dissociation equilibrium of [3]-pseudorotaxane species.

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PC-11

APPLICATIONS OF SONOCHEMISTRY FOR THE SYNTHESIS OF FUEL CELL CATALYSTS

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We report on the application of sonochemistry to the syntheses and modification of various nanoparticles with electrocatalytic activity for fuel cell applications. Sonication of a solution can generate an extremely high energy environment with up to 5000 K and 20 kPa. Sonochemistry, therefore, has been explored as a means to generate nanomaterials. We have used this technique to obtain various nanoparticles of WC_{1-x}, $Pt_{shell}Co_{core}$ alloy, $Pt_{shell}Fe_{core}$ alloy, $Pd_{shell}Co_{core}$, and Au. These nanoparticles show interesting properties and some of them outperform the nanoparticles synthesized by other methods. We found that sonication of $W(CO)_6$ in hexane produced WC_{1-x} nanoparticles, which could not be synthesized by any other methods. WC_{1-x} nanoparticles show a weak activity for the hydrogen oxidation reaction (HOR) in an acidic condition. However, when combined with Pt or Pd nanoparticles, WC_{1-x} nanoparticles enhance the HOR activity of these nanoparticles indicating a hydrogen spill-over effect [1,2]. Sonochemical treatment on an ethylene glycol solution of Co and Pt reagents turned out to be an efficient method to produce core-shell-like Pt-Co and Pt-Fe nanoparticles with Pt-enriched surfaces. These core-shell-like Pt-Co and Pt-Fe nanoparticles showed enhanced activity for oxygen reduction reaction (ORR) in an acidic condition. By controlling the times of addition of Co and Pd reagent in a reacting solution while sonicating the solution, we were able to obtain core-shell-like Pd-Co nanoparticles with various Pd/Co ratios. The Pd_4Co core-shell-like nanoparticles show the highest ORR activity among the samples we studied. We also found that sonication treatment on Au nanoparticles could induce the surface melting of the Au nanoparticles without inducing their aggregation. As a result, we could obtain Au nanoparticles whose surfaces are enriched with low-coordination number Au atoms. Such activated Au nanoparticles show remarkably enhanced HOR activity [3]. When properly combined with WO_3, the ORR performance of the sonochemically treated Au nanoparticles was enhanced to the level comparable to that of Pt nanoparticles.

In this talk, the details of the syntheses, characterization, and the catalytic properties of these nanomaterials will be presented.

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A MEDIATORLESS HIGH-POWER GLUCOSE BIOFUEL CELL IMPLANTED IN AN ANIMAL

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The design of biofuel cells involves the application of enzymes or microorganisms as catalyst for the targeted oxidation and reduction of specific fuel and oxidizer substrates to generate an electrical power output. Biofuels such as glucose can be found in physiological fluids, opening thus the way to energy harvesting from body fluids for supplying biomedical electronic devices[1]. We investigated the efficient wiring of enzymes in a carbon nanotube conductive matrix for the fabrication of a GBFC. Direct electron transfer between laccase at the biocathode and glucose oxidase at the bioanode was evidenced. The mediatorless GBFC delivered, *in vitro,* a maximum power density up to 1.3 mW cm^{-2} and an open circuit voltage of 0.95 V (50 mM glucose, 25 °C, pH 7). Moreover, the GBFC was successfully implanted in rats by surgical insertion into the retroperitoneal space, enabling Glucose and O_2 from the Extracellular Fluid to flow into the GBFC. The implanted GBFC delivered a maximum power density of 0.25 mW cm^{-2}, 0.42 mW mL^{-1} and an open circuit voltage of 0.85 V.

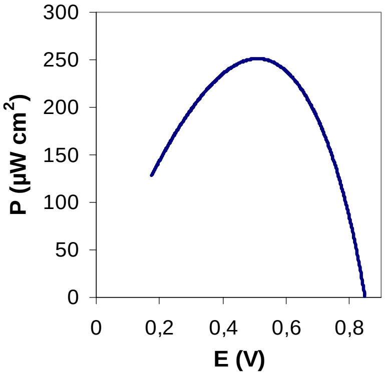

Figure. Power-voltage profile of a GBFC implanted in a male Wistar rat

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ELECTROCHEMICAL CHARACTERIZATION OF NiAl LAYERED DOUBLE HYDROXIDES PREPARED BY SOLVOTHERMAL PROCESS

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Layered double hydroxides (LDHs) constitute a family of layered compounds in some way complementary to cationic clays. They are formed by brucite-type $M(OH)_2$ layers, in which a partial M^{3+}/ M^{2+} substitution has taken place. The positive charge of the octahedral layers resulting from this substitution is balanced by the presence of interlayered anions. These interlayers are constituted of anions and water molecules which fill up all available sites. A wide variety of metal cations (MII = Ni^{2+}, Mg^{2+}, Zn^{2+}…; MIII = Al^{3+}, Ga^{3+}, Cr^{3+}…) and interlayer species (inorganic or organic anions) can be involved in the LDH structure [1]. Due to this versatility of composition and their intrinsic properties, there is an intense interest in the use of LDH for advanced applications in catalysis, separation, biotechnology and electrochemistry. For instance, redox active NiAl–Cl LDH has electrocatalytic properties for the oxidation of primary alcohols, sugars, amines and pesticides (1). They are also used in energy conversion (2).

Recently, we have developed a new amino acid assisted solvothermal process to prepare NiAl-LDH (represented by a general formula, $[Ni_{1-x} Al_x (OH)_2]^{x+}(CO_3^{2-})_{x/2}\cdot mH_2O$. This novel method involves the thermolysis of metal cations coordinated by amino acid in strong basic conditions (3). Original three-dimensional nanostructures of Ni_2Al-LDH such as flower, pompon or disk-like morphologies can be prepared (Fig.1). The electrochemical behavior of Pt electrode modified with these as-prepared NiAl phases was studied by cyclic voltammetry, as thin films coated on Pt electrode or within a µcavity electrode. The aim of this work was to correlate the morphology, the microstructure and the electrochemical properties of the three different phases $Ni_2Al-CO_3^{2-}$.

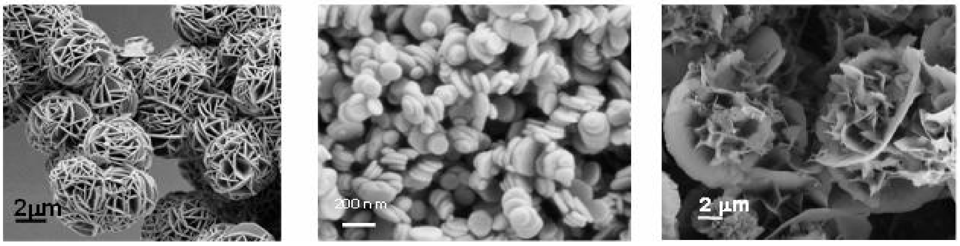

Fig.1: SEM images of NiAl-LDH phases obtained using different Glycine/Nickel ratios.

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Acknowledgment: C. M. thanks Vincent Vivier (UMEC) for providing us µelectrodes.

NANOELECTRODE ENSEMBLE BASED ON MULTIWALLED CARBON NANOTUBES IN POLYMETHYLMETHACRYLATE FILM

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Nanoelectrodes ensembles (NEEs) are new nanoelectrochemical elements that are very promising for electroanalysis, sensors and high energy chemical batteries applications [1].

The main goal of the present paper is to design NEEs both for the fundamental electrochemical studies and for the construction of the sensor elements. The later are based on immobilization of multi-wall carbon nanotubes (MWCNT) into polymethylmethacrylate (PMMA) films at glassy carbon (GC) electrode as a substrate by spin-coating technique.

Electrochemical measurements were carried out using home-made analyzer ELAN-2 [2] in electrochemical cell with the MWCNT film modified working electrode, a platinum counter electrode, and Ag/AgCl reference electrode. A 0.1 M $NaClO_4$ solution was used as supporting electrolyte and $Ru(NH_3)_6^{2+/3+}$ as a well known reversible redox couple.

The cyclic voltammograms (CV) of $Ru(NH_3)_6^{2+/3+}$ couple oxidation/reduction at the GC electrodes modified by PMMA film, diamond-like carbon (DLC) and MWCNT/PMMA film were obtained. Peaks of $Ru(NH_3)_6^{2+/3+}$ redox processes were obtained at the GC and DLC electrodes. These have been caused by semi-infinite diffusion-controlled redox processes characteristic for the conventional macroscopic dimension electrodes. While at the film electrodes prepared with a low content of MWCNT (i.e., 2.0 μg/mL) in the PMMA matrix CV has sigmoidal-shaped response with a very slight hysteresis between the forward and backward sweeps. This may be due to a well separation between diffusion layers of individual MWCNT nanoelectrodes exposed into the solution so such electrodes behave as a NEEs. After increasing the content of MWCNT NEEs are operating in a total-overlap regime. In this regime the diffusion layers at the individual electrode elements overlap to produce a layer corresponding to the entire geometric area of the NEEs. So enhanced electroanalytical detection limits for $Ru(NH_3)_6^{2+/3+}$ can be reached comparing to NEEs with low MWCNT content. This is because the Faradaic current is proportional to the total geometric area of the NEEs, while the double-layer charging background current - to the sum of the areas of the electrode elements in the NEEs. As a result, the ratio of the Faradaic-to-background currents can be several orders of magnitude higher at the NEE than at the macroelectrode. This enhancement results in a corresponding decrease in the detection limits at the NEEs. Therefore, the MWCNT-based NEEs prepared here can be useful for nanoelectrochemical studies and for practical electrochemical applications (environmental sensors for trace contents of hazardous organic chemicals detection in water samples and electrode materials in high energy chemical batteries).

The work was supported by Science and Technology Center in Ukraine projects ##4495 and 5067 (Project manager Prof. Mykola Rozhitskii).

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POLYMER-GRAFTED PLATINUM NANOPARTICLES FOR ELECTROCATALYTIC OXIDATION OF H_2O_2: TOWARD NEW ENZYMATIC NANOBIOSENSORS

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This study focuses on the electrocatalytic properties of Langmuir-Blodgett (L.B.) thin film structures based on polymer grafted platinum nanoparticles (PAA-PtNPs) toward H_2O_2 oxidation. The nanoparticles are obtained from 4-mercaptoaniline functionalized platinum nanoparticles with 2 nm averaged core size, which are chemically modified to perform *surface*-radical controlled polymerization. This leads to the formation of a polymethacrylate corona that could be further converted to poly(methacrylic acid). These elementary bricks (PAA-PtNPs) are used to form versatile mixed L.B. films with or without the addition of non redox active fatty molecules (AcB) which allows the mixed LB films structures to be built up in a reproducible way. This approach results in the formation of L.B. nanostructures in which both the number of layers and the amount of PAA-PtNP in each layer may be varied.

The nanostructures feature depends strongly on the amount of PAA-PtNPs. High PAA-NPPt content leads to quite large polymer/nanoparticle domains resulting from a large coverage density of the substrate. In opposition, low surface coverage of platinum gives small size polymer/platinum domains with a finely divided nanostructure. The electrocatalytic efficiency towards H_2O_2 oxidation depends on the presence of the AcB and on the platinum loading. We observed that the current densities increase when the PAA-PtNPs amount decreases. We attribute this change to a modification of transport matter as a function of the film nanostructuration.

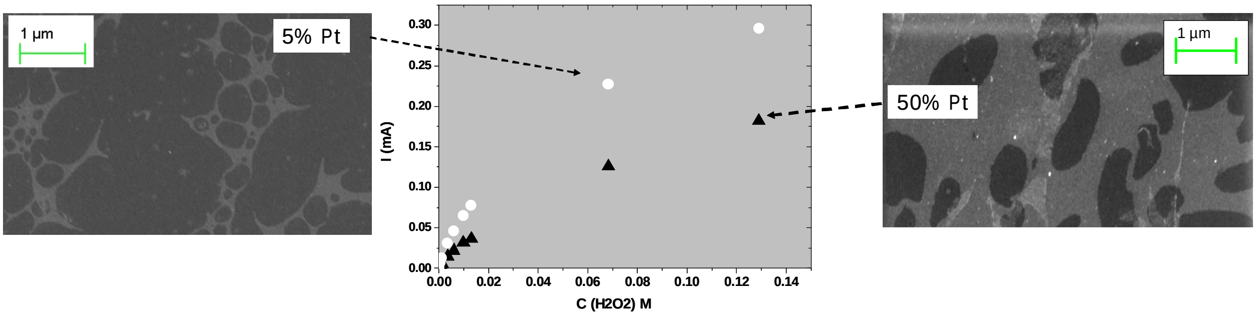

Figure: Current as a function of [H_2O_2] (potentiostatic mode E=0.5V~~) and the PAA-PtNPs~~ surface ratio. **Pictures**: SEM characterization where bright areas are relative to the PAA-PtNPs

Besides this interesting result, we plan to use these new building blocks as transducing element in enzymatic biosensor. Indeed, the grafted polymer chains contain carboxylic acid groups, which could form activated ester for further enzyme linkage. Nanobiosensors could then be synthesized in homogeneous medium and further be organized both in 2D and 3D network leading to very sensitive sensing system.

FROM NANOWIRES TO HIERARCHICAL STRUCTURES OF TEMPLATE-FREE ELECTRODEPOSITED ZnO FOR EFFICIENT DYE-SENSITIZED SOLAR CELLS

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Zinc oxide has recently emerged as a promising alternative semiconductor material to TiO_2 with marked performance improvements of ZnO-based DSSCs (dye-sensitized solar cells) achieved during the last few years.[1-3] A new and original method for the electrochemical growth of ZnO nanocrystalline porous layers and multiscale hierarchical structures is described. The structures are designed by simply playing on the growth conditions and without any use of template or additive in the aqueous deposition bath. Two types of hierarchical structures are described combining electrodeposited ZnO nanowire arrays and a nanoporous layer: nanowires arrays covered by a conformal nanoporous layer and nanowire arrays embedded in a nanoporous layer. The design process of the two structures, noted *h1*-ZnO and *h2*-ZnO, are presented in Figure 1. The global performances of dye sensitized solar cells fabricated using the best hierarchical structures are higher than those found for nanoparticulate sol-gel ZnO films and for the two basic electrodeposited structures. The maximum energy conversion efficiency of the best *h2*-ZnO cell was 3.62%.

The wires play several important beneficial roles in the presented structures since they permit the electrodeposition of thick nanoporous ZnO films which immobilize a large amount of dye, they act as preferential electron pathways for efficient charge collection and, due to their size, they enhance the light trapping in the photoanode and hence increase the light diffusion length before its harvesting by the dye. Another interest of the proposed ZnO hierarchical structures is a synthesis as well as an applied post-growth thermal treatment performed below 150°C in soft environments which are then well-compatible with lightweight plastic flexible and other fragile substrates.

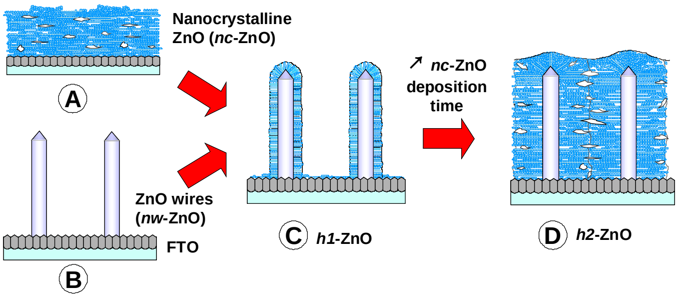

Figure 1: Schematic presentation of electrodeposited ZnO nanostructured films for DSSCs : A) Nanocrystalline porous ZnO (*nc*-ZnO); B) ZnO nanowires (*nw*-ZnO); c) ZnO nanowires decorated by a porous *nc*-ZnO layer (*h1*-ZnO); D) Same as C) obtained after longer deposition times of the electrodeposited *nc*-ZnO once that the space between the wires is filled (noted *h2*-ZnO).

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COMBINING ARYLTRIAZENES AND ELECTROGENERATED ACIDS TO CREATE WELL DEFINED ARYL TETHERED FILMS AND PATTERNS ON SURFACES

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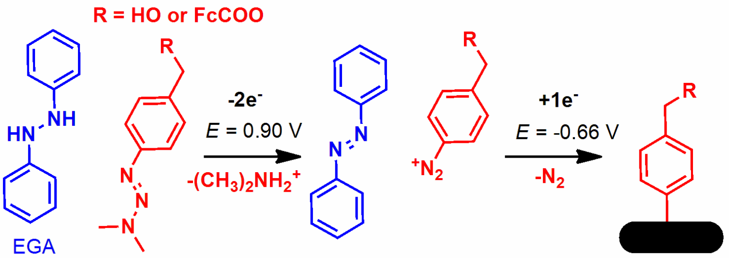
Electrografting using aryldiazonium salts is a recognized method for covalently tethering aryl groups to various conducting materials.[1] The high reactivity of aryldiazonium salts often limits the synthetic possibility of constructing complex molecules. To inhibit the high reactivity of diazonium salts a protection group could be attached to the diazonium functionality. Aryltriazenes formed by reacting the aryldiazonium salt with a secondary amine was suggested by Tour.[2] Aryltriazenes may be deprotected simply by adding an acid to give the diazonium salts. Use of aryltriazenes for grafting can be made even more versatile, when the conversion to the corresponding diazonium salt only takes place essentially during grafting and only in a thin layer close to the surface to be grafted.[3]



Immobilization of sub-monolayers to 4-5 multilayers of organic molecules on carbon surfaces is performed by in situ generation of aryl radicals from aryltriazenes. The central idea consists of oxidatively forming an electrogenerated acid of *N,N'*-diphenylhydrazine to convert the aryltriazene to the corresponding diazonium salt in the diffusion layer of the electrode. In a second step the diazonium salt is reduced at the same electrode to give a surface of covalently attached aryl groups. In this manner, various moieties tethered to the aryl groups can be immobilized on the surface. Here a ferrocenyl group is introduced as redox marker, the electrochemical signal of which is extraordinarily well defined. This is so, independent of film thickness which is easily controlled by the number of repetitive cycles performed. It is also demonstrated that the new approach is suitable for patterning of surfaces using scanning electrochemical microscopy.

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PC-18

ELECTROCHEMICAL AND SPECTROSCOPIC CHARACTERIZATION OF PROTON CONDUCTIVE MEMBRANES BASED ON SULFONIC ACID POLY(STYRENE-CO-ALLYL ALCOHOL)

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The optimization of fuel cell components such as proton conductive membranes is one of the major interests in current materials research, with special emphasis on the development of methods for obtaining and characterizing these complex systems (1). Particularly, the sulfonation of commercial polymers is pointed as one of the most promising approaches to obtain membranes exhibiting adequate proton conductivity combined with good thermal and mechanical properties (2). In the present work, electrochemical and spectroscopic characterizations of proton conductive membranes based on sulfonated poly(styrene-*co*-allyl alcohol) (PSAA-SO_3H) are presented.

PSAA-SO_3H samples were obtained in different sulfonation degrees from PSAA commercial polymer, based on a procedure adapted from Rocco and co-workers (3). Membranes of the sulfonated polymers were obtained by casting from solutions onto Petry dishes and dried under vacuum until constant weight prior to the characterizations.

FTIR spectra indicated the covalent insertion of $–SO_3H$ groups, particularly in the spectral region between 1150 and 1275 cm^{-1}, evidencing the presence of sulfonic acid in protonated ($–SO_3H$) and dissociated ($–SO_3^-$) forms. Additionally, analysis of the different spectroscopic contributions in the ν(OH) region indicates the equilibrium between these forms, which mainly depend on the water retained in the membrane (Eq 1).

$$\text{PSAA–SO}_3\text{H} + n\,\text{H}_2\text{O} \rightleftharpoons \text{PSAA–SO}_3^-(\text{H}_2\text{O})_{n-1}(\text{H}_3\text{O}^+) \qquad \text{Eq 1}$$

Electrochemical impedance spectra of the PSAA–SO_3H membranes evidenced a capacitive-resistive behavior, which can be associated with the polarization processes at the electrode-membrane interfaces and with the resistance to charge transport in the membrane. The resistance values were determined for each membrane at temperatures between 20 and 80 ^oC. Conductivity (σ) values were found in the range between 10^{-6} and 10^{-4} $\Omega^{-1}cm^{-1}$ for undoped membranes under 100% relative humidity. The membranes exhibited, in general, apparent activation energy (E_a) values higher than 10 $kJ \cdot mol^{-1}$, indicating a predominantly vehicular proton transport mechanism (4), which is probably due to the low concentration of sulfonic groups and to the high water absorption by the membranes. At a molecular level, the equilibrium described in Equation 1 accounts for the acid dissociation which produces hydronium ions, responsible for the charge conduction in the membrane.

CNPq, ProPPi/UFF

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PC-19

EXTENDED VIOLOGENS: ELECTROCHEMICAL STABILITY, PERIODICITY AND CHAOS

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Organic electrochemistry in overwhelmingly large cases encounters systems, which monotonously proceed from initial forms to final products. Observed currents are regular and well defined. Few rather curious examples of autocatalytic or autoinhibitory redox reactions deviate from such simple routes. Our previous studies encountered electrochemical oscillations in thiocyanate catalyzed indium reduction and in cationic catalyzed reduction of nitro aromatic derivative. The characteristics of those systems included the negative differential resistance (NDR) contributing to periodic electrolytic currents. Here we will present effects observed during the electron transfer to an oligomer of 'extended viologen', a compound designed with a vision to be used as a molecular conductor. Compound **1** contains five reducible repetitive bipyridinium functions, which are expected to show a communication of redox centres. Surprisingly the faradaic current in the vicinity of the first formal redox potential(s) is very irregular. Detailed study of the origin of the irregular currents showed that this redox system yields oscillations without any additional external impedance[1,2]. Hence it may be a suitable candidate for a 'molecular oscillator'. The oscillating system described here involves just a single compound. It is much simpler than other electrochemical oscillators, which usually include a redox active component and either a catalyst or an inhibitor. We interpret the observed periodic faradaic currents as a result of the coupling of the heterogeneous and homogeneous charge transfer processes. The analysis confirms the deterministic character of the chaotic behaviour, allows the determination of the Feigenbaum universality constant for prediction of transfer from periodicity to chaos and conditions for sine oscillations or stability, the last one required for electron conduction.

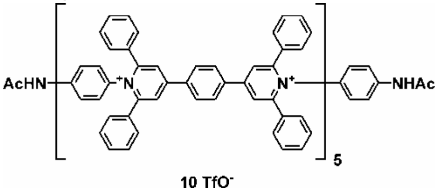

Fig. 1 Deca-cation of extended viologen **1**

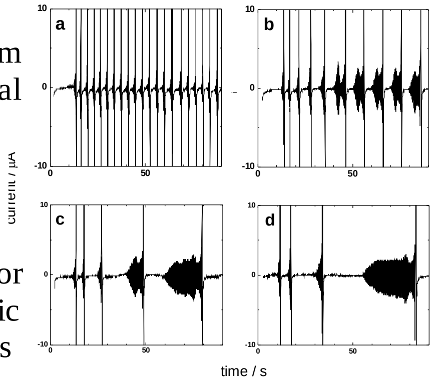

Fig. 2 Current-time series at different applied potentials

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PC-20

PECULIARITIES OF ULTRA FAST POTENTIOSTATES REALIZATION FOR NANOSECOND RESOLUTION VOLTAMMETRY

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Powerful analytical properties and wide utilization of voltammetry in different applications compel to look for this method and electrochemical instruments new possibilities while sufficient increasing rate of scanning to gigasamples per second mode. This requires lower then 1 nanosecond resolution of measurement system. Increasing of scanning potential sweep rate is limited by voltage drop on ohmic resistance of electrolyte solution. Because part of voltage is dropped in cell one obtains potentials on working electrode (WE)/solution interface different from those generated by electrochemical station (potentiostate). This phenomena influence upon obtained experimental data reliability [1].

In the paper method of voltage drop compensation that is present on ohmic resistance of electrochemical cells solution between counter and WE is considered. This method was tested in developed unit of ultra fast potentiostate (UFP) with generation of more than 1 MV/s electrode polarization rate. UFP intended for processes investigation on nanodimension electrodes (ultramicroelectrodes), including so called nanodes, operation with extremely short-time potential perturbation so that diffusion layer dimensions have nanometer size with possibility of short-time lived intermediates identification, using in scanning electrochemical microscopy [2]. Physical and technological boundaries in UFP designing using modern hardware and software basis are discussed.

In traditional potentiostate design part of electrochemical cell ohmic resistance between counter and reference electrodes is compensated by feedback loop of reference electrode for equilibrium potential measurement. For reducing resistance between working and reference electrodes the latter is mounted as close as possible to WE providing negligible small non-compensated part of resistance. Such approach is suitable until response frequency of feedback loop is greater than signal frequency. But it has technical constrains for using in traditional potensiostate on large sweep rates.

The of ohmic drop compensation method realization is based upon a feedback loop placed within one cascade of current-voltage converter in contrast to traditional scheme in which compensation circuit is used between counter and reference electrodes and crossing several cascades. This eliminates intercascade feedback loop not preferable on high frequencies, and provide necessary conditions for ultra fast modes of voltammetry.

Precision control under electrochemical processes in UFP is obtained. As A result, proposed method is very attractive for utilization in a very short-time assays, properties of different materials investigation with nanodimension resolution and in energy and energy management fields. This work was supported by Science and Technology Center in Ukraine Project ##4495, 5067 (Project manager Prof. Mykola Rozhitskii).

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ELECTROCHEMICAL GEOLOCALIZATION OF MICROBEADS POSITIONED BY OPTICAL TWEEZERS ON ULTRAMICROELECTRODE

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Electrochemistry of nano- and microparticles is of high interest for detecting single particles and also to understand the mass transport process in confined volumes. For example, the group of Compton has recently shown the sizing and locating of single particles.(1, 2)

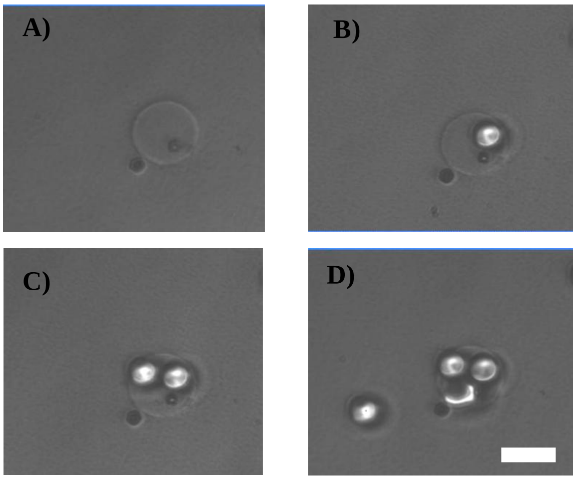

Figure. Images of a (A) naked UME on which (B) 1, (C) 2 or (D) 3 beads of radius 3 µm were deposited with the laser-based optical tweezers. Scale bar: 10 µm.

In the present work, latex micrometric beads are positioned with optical tweezers on ultramicroelectrodes (UME). Single microbeads of different radii were deposited in the diffusion layer of the UME. When a microbead is brought in the vicinity of the UME, it alters the fluxes of the redox $Ru(NH_3)_6^{3+}$ species and the corresponding diffusional shielding results in the decrease of the reduction current. Confrontation with digital simulation shows that the UME is a pertinent tool to geolocalize the beads in the vicinity of the electrode.

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CARBON NANOPARTICULATE FILM ELECTRODE FOR REDOX PROTEINS DIRECT VOLTAMMETRY AND ELECTROCATALYSIS

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Nowadays one can observe extensive interest in the development of biosensors and biofuel cell technology based on redox protein (1,2,3,4). Desired features of such devices are stability, efficiency and exhibition of direct electron transfer. Therefore the application of nanomaterials – such as carbon nanotubes (3,5), graphene sheets (3) and nanoparticles (6) which are known for their good electrical conductivity, well developed surface and are capable of immobilizing various redox proteins – could have a significant impact in developing such devices.

In this report we show that carbon nanoparticulate film electrodes are appropriate platform for immobilization of biomolecule. Modified electrodes prepared from oppositely charged carbon nanoparticles (ca. 9 to 18 nm diameter) by a layer-by-layer approach (7) are suitable for this purpose. The electrodes are prepared by immersion and withdrawal of indium tin oxide plates into suspensions of positively and negatively charged particles. The electrodes were thoroughly characterised by SEM, AFM, cyclic voltammetry and impedance spectroscopy. The electrochemical experiments were done in the presence of model reactants such as $Fe(CN)_6^{3-}$, $Ru(NH_3)_6^{3+}$, glucose and H_2O_2.

The thickness of the film depends on the number of immersion and withdrawal steps and reaches 300 nm for thickest film. The resistance of the film is ca. 300 ohms. The direct voltammetry of myoglobin (Mb) and glucose oxidase (GOx) adsorbed on the modified surface is observed. The biocatalytic activity of Mb and GOx in the carbon nanoparticulate film is also exemplified by the reduction of hydrogen peroxide and oxidation of glucose, respectively.

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NITRILE FUNCTIONALISED OLIGO AND POLYTHIOPHENES: SYNTHESIS AND STUDY OF THE METAL COMPLEXATION - ABILITY

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The synthesis and the complexation properties of β-sulfanylheptanenitrile functionalised oligo- and polythiophenes reported in are studied by means of electrochemical and spectroscopical (UV/Vis) techniques.

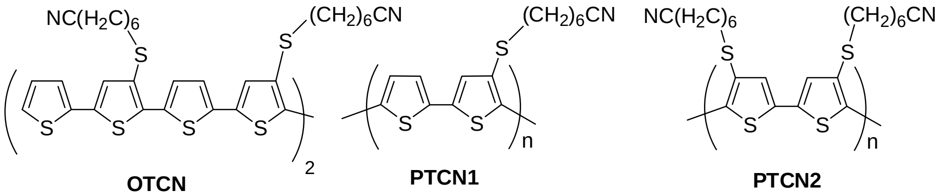

Fig. 1 The oligo (OTCN) and polythiophenes (PTCN1, PTCN2) studied.

The ability of PTCN1, PTCN2 and OTCN towards the complexation of different transition metals is compared. For, their complexation-ability is a crucial property in view of possible applications of these materials as chemical sensors for metal ions detection[1] or as carbon substitute materials for catalyst support for oxygen reduction or methanol oxidation in direct methanol fuel cells[2] (DMFC). The experimental results are compared and discussed in comparison to theoretical (DFT) calculations.

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FUEL CELL TESTING OF Pt-Ru CATALYSTS SUPPORTED ON DIFFERENTLY PREPARED AND PRETREATED CARBON NANOTUBES

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Proton-exchange membrane fuel cell (PEMFC) testing of Pt-Ru catalysts supported on differently prepared multiwall carbon nanotube (MCNT) supports was performed to elucidate the influence of the different supports on the operating characteristics of the catalysts under real direct methanol fuel cell (DMFC) anode and H_2-PEMFC anode conditions. The MCNTs were either thin, entangled or thick, disentangled. Pretreatment of the MCNTs was also done and it was either high-temperature KOH etching or annealing (graphitization)[1]. The performance of the catalysts was compared against the performance of a commercial Pt-Ru catalyst supported on a high-surface-area carbon black.

Among the different MCNT supports, the graphitized, entangled support offered the best performance in all tests, which was equal to the performance of the commercial catalyst, despite the MCNT catalyst layer was at least three times thicker than the carbon black catalyst layer. This confirmed the expected potential of nanotube supports for providing superior reactant transport properties of the PEMFC catalyst layers.

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NANOSTRUCTURED SURFACES FOR BIO-APPLICATIONS.

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Electrogenerated Chemiluminescence (ECL) is a redox-induced emission.[1] ECL is the processes whereby species generated at electrodes undergo high-energy electron transfer reaction to form excited states that emit light. Since its first application, the ECL technique has become a very powerful analytical tool and has been widely used in biosensor transduction.[2] The ECL presents an intrinsically low noise and high sensitivity; moreover, the electrochemical generation of the excited state prevents scattering of the light source: for all these characteristics, ECL is an elective technique for ultrasensitive immunoassay detection.

The majority of ECL systems involve species in solution where the emission occurs in the diffusion layer near to the electrode surface. Over the past few years, an intense research has been focused on the ECL generated from species constrained on the electrode surface.

Nowadays, more and more attention has been paid to ECL biosensors functionalized with nanomaterials due to the combination of the unique physical and chemical proprieties of the nanomaterial with the excellent aforementioned properties of ECL. In this context, the composite materials based on carbon nanotubes (CNTs) are particularly promising for sensing applications. In fact, an improvement in sensitivity and stability of ECL biosensors was obtained from the modification of the electrode surface with CNTs. Moreover, proteins and enzymes can be easily immobilized within or on the CNTs either by physical adsorption or covalent binding, often involving the carboxylic functionalities introduced onto the CNT surface by oxidizing procedures.

In the present research we combined ECL transduction with the CNTs binding proprieties in order to design a new platform for the detection of Palytoxin (PTX). Palythoa toxica, is known as one of the most potent marine toxins: human illness and fatalities have been reported after ingestion of PTX-contaminated tropical and subtropical fish and crabs.[3]

Due to the high toxicological potential of PTX and its analogs we have focused the present research on the realization of an electrochemiluminescent sensor device for the PTX detection; wile our platform is extremely versatile and can be modified to detect many other biological analyte.

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ELECTROGRAFTING OF PYRIDINE FOR ELECTROCHEMICAL APPLICATIONS

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The modification of surface by reduction of diazonium salts has attracted a lot of interest in the past decade. This method, developed by Pinson et al.[1], is very attractive because several molecules can be used to form a covalent bond between aryl groups bearing a desired functionality and different substrates. In a recent study, it has been shown that a covalent bond between glassy carbon and pyridine could be obtained by electroreduction of an diazonium salt [2]. The aim of the present work is to investigate the electrografting of pyridine from the corresponding diazonium and the electrochemical behaviour of the grafted pyridine.

In this work, a covalent bond between glassy carbon and pyridine was obtained in two steps. Firstly, the diazonium cations were synthesized in the electrochemical cell by reaction of 3-aminopyridine with $NaNO_2$ in aqueous HCl [3]. Secondly, glassy carbon electrodes were modified by electrochemical reduction of the *in situ* generated 3-aminopyridinium cations under several conditions. The effect of the glassy carbon electrode modification conditions like diazonium cations concentration and diazotization reaction time, grafting time and potential of potentiostatic reduction were investigated.

The resulting modified electrodes were characterized by cyclic voltammetry experiments, carried out in a 5 mM $Fe(CN)_6^{3-/4-}$ aqueous solution. This method has been used to confirm and to determine the barrier properties of the deposited layers and estimate the pKa of the immobilized pyridine. X-ray photoelectron spectroscopy (XPS) was used to evaluate the atomic concentration of the species present at the glassy carbon electrode surface. Cyclic voltammetry experiments showed that the blocking effect of the grafted layer increases as the applied potential is made more negative and as well with an increase of the reduction time. It is possible to obtain a relative control of the layer thickness by changing the applied potential and the grafting time. The evolution of the peak current as a function of the solution pH for the electrochemically modified electrodes in the solution containing $Fe(CN)_6^{3-/4-}$ as redox probes was investigated. Analyses revealed that the apparent pKa of the immobilized pyridine could be estimated at 5.3. Finally, the electrochemical behaviour of the pyridine-modified electrode will be discussed.

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ZINC NICKEL COATINGS OBTAINED IN THE PRESENCE OF CADMIUM AND BORIC ACID

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Steel plate can be protected from corrosion by nickel deposit. To enhance the protection, zinc is added to nickel. The best molar ratio is very difficult to obtain because of a phenomenon called anomalous codeposition [1]. It has been shown that anomalous codeposition[2] can be minimized by using boric acid [3] combined with cadmium.

Boric acid favours deposition of zinc-nickel coatings with a homogeneous phase structure (Ni_5Zn_{21}), whereas cadmium minimizes zinc deposition leading to a codeposition where the coating contains a higher nickel percentage. Boric acid raises current efficiency of the deposition process by blocking surface sites for hydrogen evolution.

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ELECTROSYNTHESIS: A SMART WAY FOR THE ONE-STEP PREPARATION OF METALLIC AND BIMETALLIC NANOPARTICLES ON CONDUCTIVE SURFACE

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In recent years considerable attention has been drawn to the deposition of metal nanoparticles onto conducting substrates due to its great importance in the fabrication of practical devices such as heterogeneous catalytic systems (i.e. application in fuel cell), electronic sensors, and biosensors [1-3]. Several methods have been reported to accomplish this purpose [4-6] among these electrosynthesis has been proved to be very striking because of the simple instrumentation and the capability to readily control the size and morphology of the as-deposited nanostructures through adjusting the electrochemical parameters [7-9].

In this report we present the electrodeposition studies of Au, Pt and bimetallic Au-Pt nanoparticles (AuNPs, PtNPs and Au-PtNPs) on Indium Tin Oxide (ITO) or and Pure Graphite Sheet (PGS) surfaces. The effect of some variables as the presence of additives (*i.e.* KI or surfactants), the electrodeposition time, the kind of precursor (*i.e.* Gold(III)-Aminoethyl Imidazolium Aurate Salt) or the precursors molar ratio (*i.e.* Au and Pt) employed, on the nanoparticles size and distribution, have been also investigated. Morphological observations have been carried out using CVs, SEM, UV-Vis spectroscopy and XRD patterns. Finally, the electrocatalytic activity towards Methanol (MeOH) oxidation in alkaline or acid medium has been studied as dependence of the different morphology. This study could offer a new approach to cost-effective electrodeposition of metal nanoparticles with excellent electrochemical properties.

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SILICON NANOWIRES IN POLYMER NANOCOMPOSITES FOR PHOTOVOLTAIC HYBRID THIN FILMS

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Hybrid thin films combining the high optical absorption of a semiconducting polymer film and the electronic properties of silicon fillers have been investigated in the perspective of the development of low cost solar cells. Bulk heterojunction photovoltaic materials based on blends of a conjugated polymer Poly (N-vinylcarbazole) (PVK) as electron donor and silicon nanowires (SiNWs) as electron acceptor have been studied. Composite PVK/SiNWs films were cast from a common solvent mixture. UV-visible spectrometry and photoluminescence of the composites have been studied as a function of the SiNWs concentration. Photoluminescence spectroscopy (PL) shows the existence of a critical SiNWs concentration of about 10 wt % for PL quenching where efficiency charge separation is obtained. The photovoltaic effect was studied under illumination. A degradation of the open-circuit voltage V_{oc} and short-circuit current density is observed at high SiNWs concentration. These results are correlated to the formation of aggregates in the composite leading to recombinations of the photogenerated charges competing with the dissociation mechanism.

CHARACTERIZATION OF MIXED SELF-ASSEMBLED MONOLAYERS FORMED UNDER POTENTIAL ASSISTED DEPOSITION.

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The formation of binary self-assembled monolayers (SAMs) with predictable composition by using the method of spontaneous adsorption from a solution of the thiol derivatives is very difficult. Usually, the surface composition is controlled by changing the ratio of the two thiols in the bathing solution for preparing the SAM, although there has not been found an exact correlation between the solution and monolayer composition. Important factors that affect the composition such as the kinetics of adsorption and the fact that the more stable thiol gradually replaces the second component need to be taken into account.

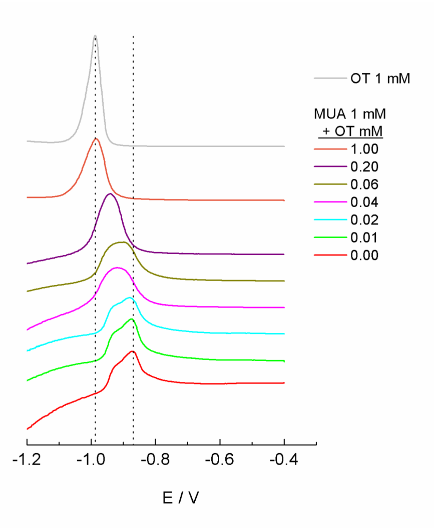

Figure. Voltammetric curves for the electrochemical deposition of mixed monolayers of MUA and OT at different solution composition.

In this work we present some electrochemical results obtained from a study on the characterization of a binary SAM composed by 11-mercaptoundecanoic acid (MUA) and octadecanethiol (OT) under potential assisted deposition from a bathing solution containing different MUA:OT ratios. We take advantage of the different adsorption potential of these molecules (Figure). As can be observed, the voltammetric curves for the oxidative deposition of the mixed monolayers are comprised between these of MUA and OT.

Potentiodynamic as well as potentiostatic methods has been used to form the mixed SAMs.[1] The characterization of the layers formed has been carried out by electrochemical techniques such as cyclic voltammetry, double layer capacity and, electrochemical impedance spectroscopy.

Two advantages in comparison to the method of spontaneous adsorption have been found: a shorter modification time and a good reproducibility in the composition of the mixed SAM.

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$Zn–Ni-Al_2O_3$ COMPOSITE COATINGS OBTAINED BY ELECTROLYTIC CODEPOSITION

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Considerable efforts has been devoted over the years to provide improved corrosion protection to metallic surfaces. Zn alloys with Ni have attracted much attention because Zn-Ni coatings possess higher corrosion resistance and better mechanical characteristics in comparison with pure zinc and other zinc alloy coatings (1).

Inert particles (Al_2O_3, SiO_2, SiC etc.) suspended in a electrolytic bath can be co-deposited during electrodeposition (2). The inclusion of nanosized particles results in: (i) an increased microhardness and corrosion resistance, (ii) modified growth to form a nanocrystalline metal deposit and (iii) a shift in the reduction potential of a metal ion (3). The properties of composite coatings depend not only on the concentration, size, distibution, and nature of the reinforced particles, but also on the type of solution unsed and electroplating parameters (pH value, current density, temperature etc.).

The aim of this study is to investigate the electrochemical behavior and the anticorrosive properties of Zn-Ni alloys containing Al_2O_3 nanoparticles, deposited on carbon steel. α – Al_2O_3 possesses excellent chemical stability and good mechanical properties, such as high micro hardness and wear resistance (4-5). The Zn-Ni alloys were obtained from alkaline commercial electrolytes (pH 13) (PREFORMA 280.5, COVENTYA S.A.S). The concentration of Al_2O_3 nanoparticles was 5, 10 and 15 g/l. The corrosion parameters were determined from the open circuit potential and polarisation curves. The results obtained show that the introduction of Al_2O_3 nanoparticles in the electrodeposition bath in concentration maximum 5 g/l brought an increase in corrosion resistance of Zn-Ni coating.

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ELECTROCHEMICAL STUDY OF THE EFFECT OF RADIOACTIVE WASTE ON THE CORROSION BEHAVIOR OF SOME ALLOYS

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Nuclear fission produces radioactive isotopes, especially ^{137}Cs and ^{90}Sr. Liquid radioactive waste usually contains soluble and insoluble radioactive components -fission and corrosion products and nonradioactive substances. Radioactive species can be effectively extracted from waters using nanostructured materials such as different types of clinoptillolite and clays. They are used for the removal of heavy metals and radioactive ions from wastewaters by ion exchange and these species are safety dispose of. Iron and its alloys are used in many applications, which have resulted in studies of the corrosion effects into different aggressive environments. Zeolites could be a material barrier for nuclear waste, absorbing radionuclides arising accidentally or by corrosion of containers.

This research investigated the corrosion behavior for various alloys in waters contaminated with heavy metals. It was evaluated the performance of some nanostructured materials (clinoptillolite and zeolites encapsulated in biopolymers) in preventing corrosion of different alloys.

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PROTON COUPLED ELECTRON TRANSFER OF UBIQUINONE Q_2 INCORPORATED IN SELF-ASSEMBLED MONOLAYER

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Quinones such as ubiquinones are the electron and proton carriers in the membranes of mitochondria, chloroplasts and oxygenic bacteria. They also act as potent antioxidants. Furthermore, quinones and their reduced derivatives act as electron donors and acceptors in photosynthesis and as charge transfer complexes.[1] Therefore, the electrochemistry of ubiquinone has attracted considerable interest in order to determine their thermodynamic constants.

We present a complete study of the reduction of ubiquinone Q_2 in aqueous medium, in a large range of pH varying from 2.5 to 12.5. The short isoprenic chain ubiquinones (UQ_2) were incorporated in a self-assembled monolayer. Under these conditions, the global $2e^-$ electrochemical reaction can be described on the basis of a nine-member square scheme.

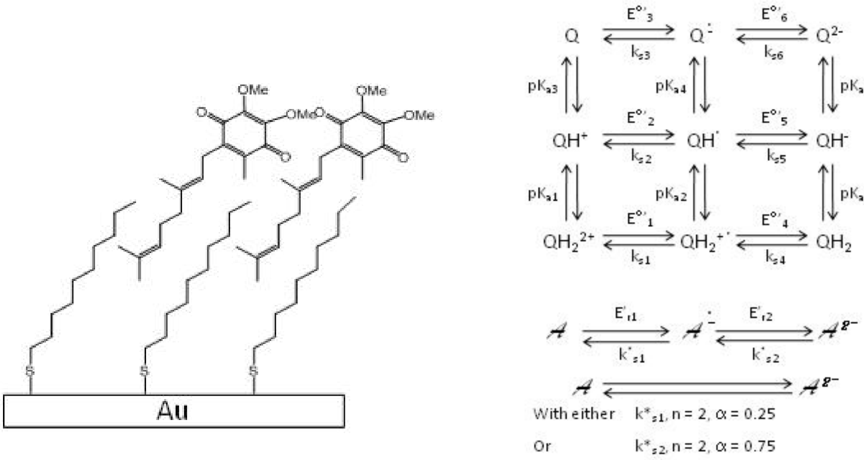

Figure 1: Left: Schematic representation of the electrode/monolayer interface. Right: The reaction scheme. The notation Q corresponds to the oxidized form of the ubiquinone Q_2.

We determined the kinetics and the thermodynamics in the light of Laviron's nine-member scheme theory.[2] A careful study over a wide pH range allowed us to deduce, for the first time, the reaction sequence in function of the different pK_{ai} and to determine the limiting rate constant.

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NEW CARBON NANOWALL ELECTRODES COATED WITH POLY(EDTA-LIKE) FILMS FOR HEAVY METAL ELECTROANALYSIS

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Monitoring heavy metal ion levels in potable water supplies is essential for human health and safety. Determination of trace levels of Cd^{2+}, Pb^{2+}, Hg^{2+} in the environment is thus a highly important, yet challenging analytical problem.

Electrochemical stripping analysis using chemically modified electrodes (CME) represents a promising method for heavy metals determination at trace levels [1]. One of the most efficient approaches towards chelating-modified electrodes consists in the direct electropolymerization of complexing monomers, leading to stable functionalized polymers films with controlled sizes and sites concentrations in a single step.

In order to utilize conductive polymers for heavy metals electroanalysis, control in morphology of conductive polymers on nano- or micrometer scales is an important issue to be investigated. Templates, for example carbon nanowalls, seem to be one of the candidates to achieve precise control in polymer morphology on such microscopic scales. Carbon nanowalls were obtained on polished stainless steel substrates by a radiofrequency plasma beam deposition method [2]. We obtained new complexing CMEs by electropolymerization of ethylenediamine tetra-N-(3-pyrrole-1-yl)-propylacetamide monomer on the carbon nanowalls layers. Thus, we achieved the synthesis of nanomaterials with tunable sizes and controlled morphologies. The complexing properties of these new nanostructurated surfaces have been evaluated for cadmium (II) electroanalysis.

Acknowledgements
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FORMATION OF BILAYER FILMS COMPOSED OF PERFLUORO-ETHER- ALKYLTHIOL AND DITHIOL SELF-ASSEMBLED MONOLAYERS AND A PFPE LUBRICANT ON COPPER SUBSTRATES.

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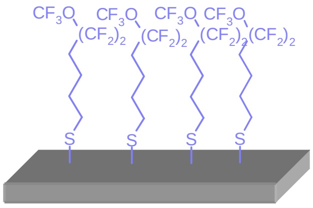
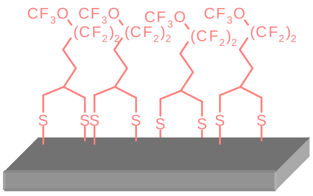
Copper is an important metal in the field of electric connectors due largely to its high electric conductivity and low cost. Having copper in its metallic state is essential for the efficiency of the connector. Indeed, the presence of an oxide layer on its surface is harmful and contributes to lower conductivity and therefore, a decrease in efficiency. Electrochemical pretreatment of copper substrate, followed by the self-assembly of monolayers of alkanethiols have been found to prevent the oxidation of the substrate metal.

Another main issue is the limited life time of the connector, due to several parameters such as copper corrosion, fretting corrosion, friction and wear of the device. To face those limitations and improve the life time of the device, a thin film of lubricant is commonly deposited on copper surface. The most common lubricants used are perfluoropolyether film (PFPE). The PFPE film has a low friction thanks its high molecular flexibility, nevertherless; this film has low adhesion on copper (especially for sub-monolayer thickness) and therefore low durability.

It is thus advantageous to graft compatible organothiol SAMs on which to deposit PFPE films and form a bilayer molecular coating that combines their properties. On the one hand the SAMs is strongly grafted on the copper substrates in its metallic state and, on the other hand, the supernatant PFPE film provides the required lubricating properties.

The present work constitutes a major progress in the field of SAMs derivated on alkanethiol on copper. The stability of the coating, which is essential for long term applications, is increased by the use of bipodal molecules. First, the perfluoro ether derivated thiol and dithiol monolayers are formed on copper surface to investigate the structural and electrochemical properties of the monolayer. A thin film of PFPE lubricant has then been deposited on the different coatings and the wetting and friction of the bilayer system have been evaluated.





Characterizations of the SAMs are carried out using contact angles, XPS, PM-IRRAS, AFM and electrochemical studies (CV, LSV, SECM).

Acknowledgements: J. Denayer is grateful to FNRS-FRIA fellowship.

ELECTROCHEMISTRY CHARGE TRANSFERS INTO NANOSTRUCTURED MEMBRANES BASED ON CALIX [4] ARENE DERIVATIVE

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Organic conducting materials have been studied extensively due to fundamental interests in reaction mechanisms as well as for their possible applications to practical devices including energy storage devices, electrochemical/chemical sensor, electrochromic devices and others. Due to their recognition properties and their efficiency for detection toxic metals, calixarene have already application in the design of chemical sensors using an electrochemical transduction.

In this study, a calix [4] arene molecular platform has been functionalized by the presence of chromophores at the upper rim and an amide group at the lower rim. This azo-calix[4]arene derivative is used as the bulding block of a nanostructured electroactive membrane. A new electrochemical sensor hhas been developed by deposition of the modified calix[4]arene on a gold electrode by spin coating. The morphology of the nanostructure materials has been studied by scanning electron microscopy (SEM). Electrochemical impedance spectroscopy (EIS) is used to study the charge transfer mechanism of lanthanide ion Eu^{3+} into the porous organic membrane. The impedance behavior of the structures was modeled by an equivalent circuit using the Z-View Software. The variations of the membrane resistance (R_m) and of the charge transfer resistance (R_{tc}) at the interface versus the concentration of lanthanide ion provide a way for the detection of lanthanides. Efficient charge transfers between the nanostructured material and fullerene have also been obtained, offering new opportunities for photovoltaic applications.

PREPARATION AND CHARACTERIZATION Nb-TiO$_2$ SUPPORTED PLATINUM NANOCATALYST FOR OXYGEN REDUCTION REACTION IN ALKALINE SOLUTIONS

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Platinum based nanocatalyst at home made Nb-TiO$_2$ support was synthesized and characterized as the catalyst for oxygen reduction reaction in 0.1 mol dm^{-3} NaOH, at 25^{0}C. Nb doped TiO$_2$ catalyst support, containing 5% of Nb, has been synthesized by modified acid-catalyzed sol-gel procedure in non-aqueous medium proposed by Boujday et al. (1). BET and X-ray diffraction (XRD) techniques were applied for characterization of synthesized supporting materials. Surface area and pore size distribution of the catalyst support were determined from adsorption isotherm of nitrogen, applying gravimetric McBain method. XRD analysis revealed only a presence of anatase TiO$_2$ phase in synthesized support powder. Existence of any peaks belonging to Nb compounds has not been observed, indicating Nb incorporated into the lattice.

Nb-TiO$_2$ supported Pt nanocatalyst, was synthesized using borohydride reduction method (2). Synthesized nanocatalyst was characterized by TEM and HRTEM techniques. It was found quite homogenous platinum nanoparticles distribution over the Nb doped TiO$_2$ support with mean particle size of about 4 nm. High resolution TEM micrographs revealed no pronounced particle agglomeration. Electrochemically active surface area of Pt for Nb-TiO$_2$/Pt catalyst was determined from adsorption/desorption charge of hydrogen atoms, after double layer charge substraction, taking the reference value of 210 μC cm^{-2} for a charge of full coverage with adsorbed hydrogen species at Pt.

Electrochemical techniques cyclic voltammetry and linear sweep voltammetry at rotating disc electrode were applied in order to study kinetics and estimate catalytic activity of this new catalyst for the of oxygen reduction reaction in alkaline solution. Two different Tafel slopes were found: one close to 90 mV dec^{-1} in low current density region and other close to 200 mV dec^{-1} in high current density region, which is in good accordance with literature results for oxygen reduction at Pt catalysts in alkaline solutions (3,4). Small enhancement in specific catalytic activity (expressed in term of kinetic current density per real surface area) of Nb(5%)-TiO$_2$/Pt catalyst for oxygen reduction reaction in comparison with the carbon supported platinum (Vulcan/Pt) nanocatalyst, was found.

Keywords: Nb-TiO$_2$ support, Nb-TiO$_2$/Pt catalyst, Pt nanoparticles, oxygen reduction reaction, alkaline solutions.

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SCANNING ELECTROCHEMICAL MICROSCOPY AS A USEFUL METHOD TO EVIDENCE THE SMALL PHOTO-INDUCED ACTIVITY OF ULTRA-THIN AMORPHOUS TiO_2 FILMS.

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Thanks to its photocatalytic and photo-induced hydrophilicity, crystalline titanium dioxide (mainly in the anatase form) is increasingly encountered in self-cleaning applications. Amorphous TiO_2 films with thicknesses comprised between 7 and 50 nm have been deposited by reactive magnetron sputtering on paint-coated steel substrates. Despite the nanometer scale of this thickness range, a photo-induced response has been detected electrochemically by scanning electrochemical microscopy (SECM) versus the thickness and crystalline or amorphous nature of the films. By using the reduction signal of dissolved oxygen at the vicinity of the film surface in an aqueous media, it has been possible to evidence the weak photo-induced reactivity of XRD-amorphous films. Despite the low reactivity observed for such amorphous TiO_2 layers as compared to crystalline anatase films, SECM could be pointed out as a promising technique to rank moderate or low photocatalytic properties of thin films of TiO_2, more sensitive than colorimetric or degradation tests. Here, the weak photoactivity detected on the paint-coated substrate allows to induce hydrophilic properties for self-cleaning operations without damaging the substrate.

TOPOLOGICAL CONTROL OF THE DISSYMMETRIC MODIFICATION OF CARBON TUBES WITH PLATINUM BY BIPOLAR ELECTROCHEMISTRY

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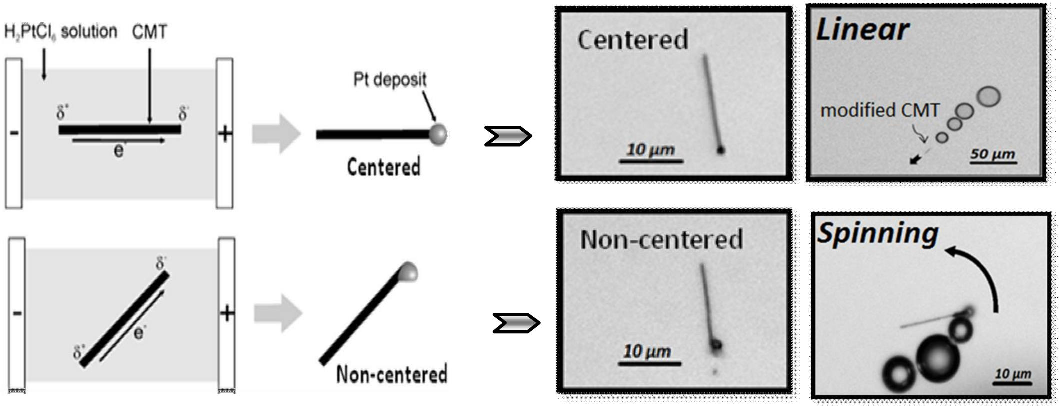
Designing micro- and nanomotors with a specific and controlled motion is one of the big challenges in the field of nanotechnology. Different approaches have been reported to prepare dissymmetric objects at the micro or nanometer scale in order to carry out localized catalytic reactions and induce the desired motion. But the majority of the current methods are rather complex and based on interfaces to generate the necessary dissymmetric objects.[1]

In the present study we applied the concept of bipolar electrochemistry in a bulk solution to synthesize dissymmetric carbon microtubes (CMTs).[2,3] Platinum metal was electrodeposited at one end of the CMTs with two different topologies, catalyzing the decomposition of hydrogen peroxide (chemical fuel) into water and oxygen bubbles and generating a propulsion.[4] Two topologies of Pt clusters have been identified, corresponding to a centered and non-centered deposit with respect to the tube axis. This difference was attributed to the orientation of CMTs in the electric field at the beginning of the electrodeposition process, because the nucleation starts at the point of maximum polarization. As a result of these two topologies a linear (for centered) and spinning (for non-centered) motion can be induced.



A) CMT alignment scheme and the resulting topology. B) Obtained CMTs with corresponding motion.

Controlling the alignment of CMTs during the bipolar electrodeposition by changing the viscosity and/or the applied potential allows to generate selectively one topology and as a consequence also the associated motion.

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STEADY STATE FLUORESCENCE STUDIES ON ELECTRODEPOSITED ZnO-BASED HETEROJUNCTIONS

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A study about fluorescence phenomena in hybrid systems based on electrodeposited zinc oxide (e-ZnO) such as ITO/e-ZnO/P3HT (P3HT = poly 3-hexylthiophene) and ITO/e-ZnO/P3HT:PCBM (PCBM = [6,6]- phenyl C60 butyric acid methyl ester) is performed in order to give a contribution to research about hybrid solar cells (1). Fluorescence studies give information about the efficiency of a photovoltaic device; in fact photoluminescence (PL) quenching is a consequence of an efficient photo-induced charge transfer across different layers of a solar cell.

In the above mentioned systems, the contact between ITO and ZnO has been obtained by electrochemical deposition of ZnO from a solution of $Zn(NO_3)_2$ by applying a constant potential between the working and the reference electrodes; the contacts e-ZnO/P3HT and e-ZnO/P3HT:PCBM have been obtained by spin coating the organic materials on the previously electrodeposited ZnO.

Fluorescence spectra have been recorded by applying excitations with different wavelengths perpendicularly to the samples surface. PL spectra of ZnO/P3HT and ZnO/P3HT:PCBM recorded at the excitation wavelength of λ=350 nm display peaks at around 570 nm due to emission phenomena occurring inside ZnO films. ZnO/P3HT shows another evident PL peak at 650 nm connected with emission phenomena inside the conducting polymer. ZnO/P3HT:PCBM presents a not well evidenced shoulder at 620 nm due to emission phenomena inside the blend.

At 510 nm excitation wavelength, ZnO/P3HT displays two emission peaks at 650 nm and 700 nm associated with emission inside the polymer.

By comparing photoluminescence spectra of ZnO/P3HT and ZnO/P3HT:PCBM, lower fluorescence intensity is recorded in the case of ZnO/P3HT:PCBM for both the applied excitation wavelengths, indicating a more efficient photo-induced charge transfer across the different layers of ZnO/P3HT:PCBM heterojunction.

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REDOX PROPERTIES OF FERROCENE GRAFTED ON Si(111) IN DIFFERENT MOLECULAR ARCHITECTURES.

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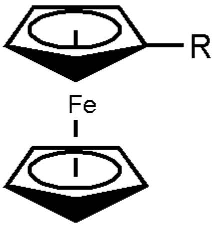
Various experimental strategies are exploited to graft the Ferrocene redox couple on the Si(111) surface: photochemical grafting, surface chemical reaction using a Pt catalyst, post functionalization Si(111) surface previously modified with undecanoic acid.



R = $-H$ (FC), $-CH_2-OH$ (MFC), $-CH=CH_2$ (VFC)

Cyclic voltammetry and electrochemical impedance spectroscopy are used to characterize experimentally the grafting process and the surface state. In particular, the dynamics of the electron transfer is assessed as a function of different Si(111) - molecular spacer - ferrocene systems.

FUNCTIONALIZATION OF GLASSY CARBON SURFACE BY MEANS OF ALKYL AND AROMATIC AMINO ACIDS. AN EXPERIMENTAL AND THEORETICAL INTEGRATED APPROACH.

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Glassy Carbon (GC) electrode surfaces are functionalized exploiting the electrochemical oxidation of six amino acids: β-Alanine, L-Aspartic acid, 11-aminoundecanoic acid, 4-Aminobenzoic acid, 4-(4-Amino-phenyl)-butyric acid, 3-(4-Amino-phenyl)-propionic acid . This procedure allows to graft (i.e. attach the amino acids on the electrode surface through the formation of a carbon–nitrogen covalent bond) the amino acids on the GC, leading to a surface layer featuring carboxylic groups facing the solution. Electrochemical (cyclic voltammetry and electrochemical impedance spectroscopy) and XPS techniques are used to characterize experimentally the grafting process and the surface state. Theoretical results are compared with the experimental evidence to determine, at a molecular level, the overall grafting mechanism. Ionization Potentials, Standard Oxidation Potentials, HOMO and electron spin distributions are calculated at the CCD/6-31G* level of the theory. Comparison of experimental and theoretical data strongly suggests that the main electroactive species is the zwitterionic form for the three alkylic amino acids, while the aromatic ones show a different behaviour: comparison between experimental (oxidation potentials) and theoretical results suggests that both the neutral and zwitterionic forms are present in the acetonitrile solution. When the electroactive zwitterionic species is considered, a rearrangement reaction, following the electrochemical oxidation, is proposed [1], where an H^+ proton transposes from the amino to the carboxylic group. This to account for the grafting process.

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CONDUCTING POLYMERS FROM “GENETICALLY MODIFIED” SPIDER-LIKE OLIGOTHIOPHENES: A COMBINED CV AND EIS INVESTIGATION

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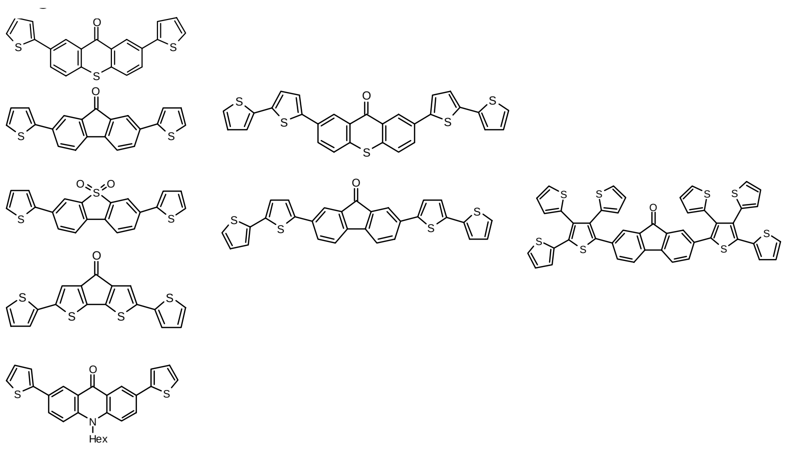
In the last years we have been introducing the attractive family of spider-like oligothiophenes, achieving reliable rationalization criteria for their structure/properties relationships[1,2]. Now we are ‘genetically modifying’ them by inserting a non-thiophene conjugated core with tunable electronic properties, with the aim of modulating both absolute and relative positions of the HOMO and LUMO energy levels, together with the electronic distribution on the main conducting backbone. Our exhaustive electrochemical investigation on a wide, systematic oligomer series has afforded interesting interpretative/predictive criteria concerning their electron properties and polymerization ability.

Now we are focusing on the characterization of the conducting films obtained by electropolymerization from the above “genetically modified” oligomers, on both GC and ITO electrodes, combining cyclic voltammetry (CV) with electrochemical impedance spectroscopy (EIS) experiments.

In particular, we will discuss combined CV and EIS results concerning the systematic series reported in Figure 1, to highlight and rationalize the effects of both the length and branching of the all-thiophene conjugated side chain (at constant modified core) and the nature of the modified core (at constant side chain) on the polymer functional properties, in terms of conductivity, mass transport, charge transfer and capacitance.



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PHYSICOCHEMICAL PROPERTIES STUDY OF NEW TOLIDINE BASED-COPOLYMER SYNTHESIZED BY DIFFERENT METHODS

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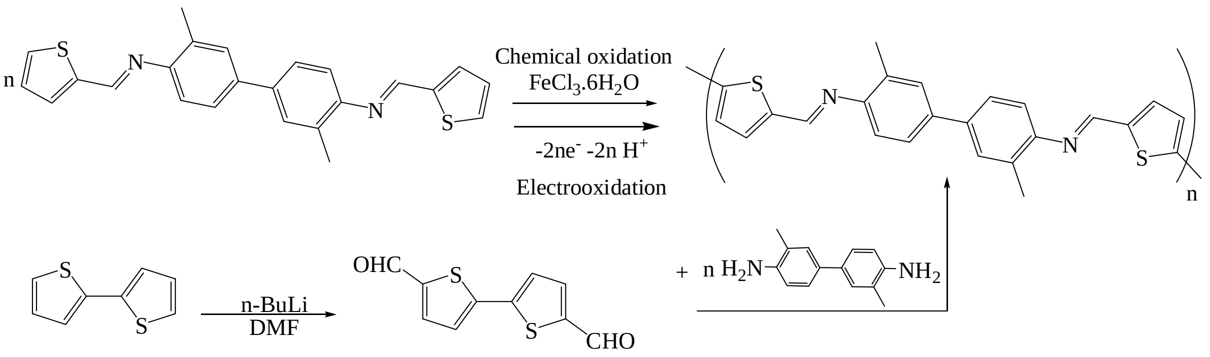
A new 4,4''-bis(2'-thienylideneimino)-3,3''-dimethylbiphenyle monomer (TOT) based on o-tolidine functionalized by two thienyls as terminal residues was synthesized, characterized by the usual spectroscopic methods and then polymerized using chemical and electrochemical oxidation to produce a bithiophene-tolidine based-copolymer material. Besides, and for comparison purposes, the polycondensation (PC) of the o-tolidine and 2,2'-bithiophene-5,5'-dicarbaldehyde was carried out to produce the same copolymer.



When TOT is oxidized electrochemically, we obtain a copolymer which is soluble only in the dimethylsulfoxide solvent of the electrolytic solution [$TBAPF_6$ (0.1M)/DMSO]. The copolymer obtained by chemical oxidation is also soluble in DMSO and in dimethylformamide; whereas, the PC reaction leads to a copolymer slightly soluble in DMSO. The low solubility of the latter product is probably due to the longer chains obtained by PC method; whereas, the higher solubility of the products obtained by the oxidation methods may be due to shorter copolymer chains. According to UV–Vis measurements, the optical band gap values (E_g) of the copolymers synthesized by PC and by chemical oxidation is 2.19 eV. The thermogarvimetric and differential thermal analysis showed a high decomposition temperature of the copolymer obtained by chemical oxidation method when compared to the decomposition temperature of the copolymers obtained by oxidation methods. All the copolymers are conductive and exhibit a quasi-reversible electroactivity.

DFT AND MONTE CARLO MODELISATION OF CO OXIDATION ON A NICKEL SURFACE

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Understanding chemical reactions that take place on catalytic surfaces is of vital importance to the chemical industry. The application of molecular modelling (1) and numerical methods (2) in heterogeneous catalysis, as a complement to experimental studies, has grown rapidly in recent years.

The adsorption of carbon monoxide "CO" on transition metal surfaces, is often regarded as a benchmark system and a subject of many studies, both experimentally and theoretically.

In this work, we performed calculations at two levels of theory. Firstly, we use the Density Functional Theory (DFT) with periodic boundary conditions. To find the preferred mode (Top, Bridge or Hollow) for CO reacting on nickel surface, we previously examine its adsorption behavior on the Ni (*hkl*) surfaces.

Secondly, we use an irreversible Surface-Reaction which was well described in the seminal work of Ziff, Gulari and Barshad (3) to simulate a catalytic oxidation of CO on a (100) plane of a model surface represented (internally) by a rectangular matrix. It is important to note that, despite its simplicity, the so called Ziff-Gulari-Barshad model allows to capture some fundamental features underlying the dynamics of surface reactions.

The Monte Carlo simulation results are thus compared to those obtained from a mathematical model which is constructed within the framework of the mean field approximation. In this respect two models are addressed, the site approximation in which correlation is totally neglected and the pair approximation which does consider spatial correlation between pairs of sites.

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NANOWIRES AND THIN FILMS OF CIS/CIGS OBTAINED BY ELECTRODEPOSITION AS ABSORBER FOR SOLAR CELLS.

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Copper indium gallium selenide (CIGS) compounds are considered among the most efficient absorber materials for solar cells applications; in fact they present relevant advantages, like high absorption coefficients of visible light (up to about 105 cm-1), facility to undergo band gap engineering through alloy composition and long-term opto-electronic stability [1]. For these features, CIGS-based solar cells compete with poly Si-based ones, and considerable efforts have been made for developing innovative devices using these materials. Up to date, the best performance was obtained by the NREL group: for a single-junction CIGS solar cell a conversion efficiency of more than 20% was achieved [2]. This device was fabricated by means of a process difficult to scale up, because it is based on a three-stage co-evaporation process that can severely hinder diffusion of this device. In order to make CIGS-based solar cells more competitive, low cost and easy scalability processes must be developed. In this context, electrodeposition can play a key role, because it is a very simple and quick technique for obtaining good-quality, large-area CIGS films compared to other fabrication methods. A further advantage of the electrochemical route is the possibility to form homo-junctions of CIGS without changing the electrolyte solution, as shown by Dharmadasa et al. [3], who also evidenced how it is possible to control simultaneously type of electrical conduction and energy gap (from 1.1 to 2.2 eV) by changing the applied voltage.

In this work, we report some preliminary results concerning the fabrication of CIGS thin films and nanowires. Thin films were deposited into a flexible substrate (PET/ITO) while nanostructures were obtained inside the channels of an anodic alumina membrane by one-step potentiostatic deposition at different applied potentials, room temperature and from an unbuffered sulphate electrolyte. Tunable nanowire length and composition was achieved through manipulation of applied potential and electrolyte composition. XRD patterns showed that in all deposition conditions CIS and CIGS compounds, whose chemical composition was determined by EDS analysis, were amorphous. The results relative to chemical composition of the electrodeposited CIGS, together with the response under monochromatic illumination, will be presented and discussed.

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THIN ZNS FILMS OBTAINED BY ELECTRODEPOSITION AS BUFFER FOR SOLAR CELLS.

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An important goal in the field of solar energy conversion is the use of highly efficient, cheap, abundant and non-toxic materials. Although silicon meets most of these criteria, high-efficiency solar cells are based on monocrystalline Si that is highly expensive. Solar cells based on thin films of semiconductors are emerging as cheaper alternatives to silicon. In particular, a record efficiency was achieved with CIGS based solar cells [1]; however, these were prepared using a very expensive method and CdS was mainly used as buffer layer.

The band-gap of this compound is about 2.42 eV: therefore light with a wavelength below 520 nm cannot be transmitted through the absorber, causing a collapse of quantum efficiency. Another issue with using the CdS is the high toxicity of Cd. For these reasons, numerous studies are undertaken to replace CdS with other not toxic buffer having a wider band gap. Among various options, ZnS is extremely interesting, because it has a band gap of about 3.74 eV, thus being transparent to most part of the solar spectrum [2]. Other interesting materials are In2S3, InSxOy, GaS, Ga2S3, Ga2O3, GaSxOy and InGaxSyOz. In particular, InSxOy, GaSxOy and InGaxSyOz buffers are very promising because of their large band gap, approximately equal to 3.5 eV [3-5].

In this work, attention was focused on the electrochemical growth of ZnS thin film on flexible substrate (PET/ITO). We report some results concerning a systematic study on the fabrication of ZnS thin film obtained by potentiostatic deposition from different electrolytic baths. In particular two different zinc salts were used, zinc acetate and zinc sulphate, with or without complexing agent, with the aim to obtain stechiometric compound.

Film characterization was performed by means of several techniques (EDS, SEM, RAMAN, XRD) giving information both on their chemical composition and structural. Preliminary results on the photoelectrochemical behavior of ZnS thin films will be also discussed.

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PC-48

APPLICATION OF LANGMUIR-BLODGETT TECHNOLOGY FOR ENHANCEMENT OF ECL DETECTION SENSITIVITY OF POLYACENES IN WATER

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Actuality of polyacenes detection in environment, most of which are carcinogenic substances, increases with the growth of number of vehicles at the roads of the cities. In Ukraine this problem is of particular importance due to considerable number of by-product-coking industry plants and low quality of motor oils. The detection of polyacenes is complicated by the fact that that they are water insoluble and exist in the form of nanodimensional species.

Previously we have proposed method of polyacenes detection based on electrogenerated chemiluminescence (ECL). Polyacenes were extracted from water by benzene and toluene and were transferred into aprotic solvents where the ECL detection was performed [1]. Use of Langmuir-Blodgett (LB) technology allows improvement of method of polyacenes ECL detection by their transfer into LB monolayer at the surface of electrode and conduction of assay in aqueous media. Conducted investigations of ECL from LB monolayers made of polemethylmethacrylate (PMMA) doped with model polyacenes (rubrene, 9,10-diphenylanthracene) [2] showed that up to $(1 | 2)\cdot 10^{14}$ cm^{-2} of polyacenes molecules can be incorporated into PMMA matrix without affecting its ordered structure. Such surface concentration corresponds to $(1.7 | 3.3)\cdot 10^{-10}$ moles of polyacenes in the analyzed sample. At the same time the analytical signal (ECL intensity) is 16 thousands times greater than the background signal. That is equivalent to corresponding reduction of polyacenes detection level in the samples.

Conducted investigations of model systems allowed determination of optimal conditions for polyacenes detection, namely: electrode material – indium-tin oxide with resistivity below 30 Ohm/cm; number of LB monolayers - 1 | 3; surface pressure during monolayer deposition - 14 | 16 mN/m; coreactant – 10 mM of tripropylamine or sodium tetraphenylborate; supporting electrolyte – 0.1 M of sodium perchlorate.

The work was supported by Science and Technology Center in Ukraine projects ##4495 and 5067 (Project manager Prof. Mykola Rozhitskii).

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STABILIZATION ROLE OF A PHENOTHIAZINE DYE ON H_2 ELECTROCATALYTIC OXIDATION VIA *AQUIFEX AEOLICUS* HYDROGENASE

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The [Ni-Fe] membrane-bound hydrogenase from the hyperthermophilic microaerophilic bacterium *Aquifex aeolicus* (Aa Hase) is a good candidate as a biocatalysts in biofuel cells, since it exhibits oxygen, CO and temperature resistances (1-3). Various attempts to immobilize hydrogenase onto electrodes have been carried out: entrapment in clay layers, with coimmobilisation of viologen molecules or polyviologen layers as redox mediator sources, biocomposite electrode based on carbon nanotube networks, thiol-functionalized gold electrodes, and recently a novel concept based on the reconstitution of the electron transfer chain into liposomes. However all the studies on H_2 electrocatalytic oxidation *via* hydrogenase led to continuous decrease in time of the catalytic current accordingly due to leaching of the enzyme. We present in this work Aa Hase immobilization on membrane coated PG electrode which prevents catalytic current decrease (4, 5). Addition of the phenothiazine dye in solution, adsorbed or electropolymerized allows to analyze direct and mediated electron transfer processes, and thus to discriminate between leaching or degradation of the enzyme. A multiple role of the electropolymerized dye is demonstrated, including redox mediator and enzyme anchoring.

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TiO_2-NANOTUBE MODIFIED ELECTRODE FOR PHOTO-ELECTROCHEMICAL BIO-FUEL CELLS

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Enzyme modified electrodes have attracted much attention due to high expectations regarding their application as catalytic electrodes in bio-fuel cells. (1) Dye-sensitised photo-anodes of metal oxides (in Grätzel cells (2)) have also attracted much interest due to high photon-to-electron conversion efficiencies and relatively low production cost (with respect to more conventional cells which are based on photovoltaic silicon devices). A combination of these technologies can create enzyme assisted photo-electrochemical bio-fuel cells that use the two original cell structures to complement each other. (3,4)

In our research TiO_2 nanostructured photo-anodes are used in combination with enzyme catalysed bio-fuel oxidation. Preparation of the photo anode includes the formation of TiO_2 nanotubes in and dye-sensitisation of the anode's surface. Visible light incident on these modified electrodes results in the photo excitation of the dye and the separation of charge. The dye is quenched by β-nicotinamide adenine dinucleotide (NADH) present in the electrolyte solution that ultimately transforms into NAD^+. (5) The catalytic oxidation of glucose within the cell in the presence of glucose dehydrogenase (GDH) replenishes the supplies of NADH from the oxidised form of this mediator, NAD^+, allowing the photo-anode reactions to continue as long as glucose is present.

The photo-electrochemical bio-fuel cell is completed by the presence of a platinum cathode – which performs reduction of oxygen to water – resulting in a potential difference and a flow of current between the terminals of the cell dependent on the intensity of the incident light. In this presentation we describe our investigation of this system; the performance of the electrochemical cell is discussed and analysed, and comparison is made with respect to existing technology.

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ELABORATION OF TANTALUM OXIDE AND CARBON NANOTUBES COMPOSITE COATINGS ON TITANIUM FOR BIOMATERIAL APPLICATIONS

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Titanium and its alloys are very commonly used as biomaterials in orthopedic and dental implants for their excellent mechanical, biological and chemical characteristics (low density, high solidity and fatigue strength, complete inertness to human body, reinforced biocompatibility and corrosion resistance). However, toxicity of alloying elements, long-term degradation and weak osseointegrative properties remain critical points [1,2].

In this context, we have considered the deposition on titanium of thin composite coatings based on tantalum oxide and carbon nanotubes by sol-gel process [3]. Tantalum is greatly appreciated for its high biocompatibility and bioactivity, as well as its strong resistance to bio-corrosion [4]. Carbon nanotubes are used for their ability to reinforce the homogeneity and compactness of the deposits, and to strengthen the interaction with bone cells by biomimicry [5,6]. Those composite layers are further modified with multifunctional organophosphonic acid molecules, able at the same time to chemically bind with tantalum oxide on the surface as well to assist and improve hydroxyapatite formation process at the interface with human body environment [7].

The global quality of these hybrid inorganic/organic coatings in terms of structural and morphological features, resistance to corrosion and *in vitro* induction of hydroxyapatite growth is assessed by XPS, SEM, TEM, peeling tests, contact angles, free potential and polarization curves.

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PC-52

ELECTRO-ASSISTED FORMATION OF ORGANOTHIOLS SELF-ASSEMBLED MONOLAYERS ON POLYCRYSTALLINE COPPER SURFACES

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Molecular films of organothiol molecules on noble (Au) and oxidizable (Zn, Cu, …) metals have been broadly studied for the last 25 years. They are well acknowledged for their ease of preparation and high reproducibility to generate robust, densely packed and greatly ordered assemblies. In particular, organothiol self-assembled monolayers (SAMs) adsorbed on polycrystalline copper can act as effective barriers against the penetration of corrosive agents to the surface. The oxidation state of copper surface is a key parameter for preparing reproducible and high quality films: several studies have clearly shown the efficiency of an electrochemical reduction pretreatment of copper to obtain well defined oriented and organized monolayers [1-4].

The classical method for generating SAMs is based on a "*passive*" adsorption process, by simply immersing the substrate into the surfactant solution for a predefined duration. Since recently, a new interesting approach, which relies on an electro-assisted adsorption mechanism, has also been investigated: by involving the interfacial electrical field, this "*active*" process allows an improved assistance and control of the molecular adsorption at the surface [5,6].

The main objective of this work consists thus in carrying an electro-assisted grafting of aliphatic thiols, dithiols and dithiocarboxylic acids on polycrystalline copper. Chelating dithiols ($R(SH)_2$) have been recognized to lead to more stable films than their thiols (RSH) counterparts. Aliphatic dithiocarboxylic acids (RS_2H) are especially interesting for applications involving temporary and removable coatings [6,7].

The quality and stability of the different SAMs are assessed by PM-IRRAS, XPS, contact angles, cyclic and linear sweep voltammetry, cathodic desorption, and SECM.

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DETERMINATION OF INORGANIC ARSENIC WITH ENSEMBLES OF NANOELECTRODES: FROM BATCH TO FLOW ANALYSIS

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Extensive arsenic contamination of drinking water has been reported in many parts of the world. Exposure to arsenic can cause a variety of adverse health effects, including carcinogenic effects (1), and the World Health Organization recommends a maximum concentration of 10 μgL^{-1} of arsenic in drinking water (2). Starting from these needs, several studies have been carried out from the electrochemical detection point of view, and anodic stripping analysis results a good technique to perform a field-deployable instrument for the detection of inorganic arsenic. Other studies showed that the use of the so called nano-electrode ensembles (NEEs) can improve the performances of electrochemical determinations thanks to dramatically improved signal to background current ratios with respect to other electrode systems (3).

In this communication, a method for the detection of As (III) at NEEs is presented. Particular attention has been addressed to the optimization of the analytical procedures. In order to lower the LOD and to increase the number of performable analysis for each NEE the right choice of the electrolyte concentration and electroanalytical parameters are crucial. By performing measurements in batch, a LOD of 2 ngL^{-1} has been achieved.

An homemade flow cell to be used as the prototype of a field-deployable device will be also presented. The device allows the easy replacement of the NEEs and the regeneration of the auxiliary electrodes. Advantages and limits of the flow analysis of As(III) will be discussed.

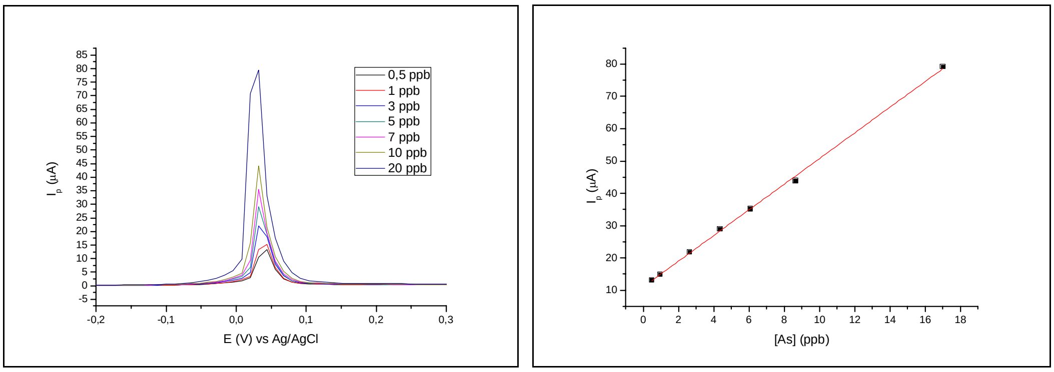

Figure 1.a-b. SWASV i-E curves recorded at NEE as a function of As(III) concentrations (a) and As stripping pick current versus the As(III) concentration (b). SWASV parameters: E_{dep}: -0,4; t_{dep}: 120 sec; incr 12mV; amplitude 75mV; frequency 250Hz.

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EFFECTS OF ANNEALING TEMPERATURES ON STRUCTURAL AND OPTICAL PROPERTIES OF TiO_2 THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION.

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Much attention has been paid these last decades to the study of titanium dioxide. In this respect, particular interest has been attached to the environmental applications of such material that is gaining in popularity day after day. Indeed, extensive studies and investigations are being conducted for various applications, namely photo-induced water splitting [1], dye-sensitized solar cell [2], environmental purification [3] etc … . The chemical and physical properties of the prepared materials depend strongly on the method used for their fabrication

In this work we report some results on the preparation of titanium oxide TiO_2 thin films by chemical bath deposition onto the glass substrates. The deposited films were annealed at different temperatures in air. The X-ray diffraction (XRD) experiments show that the well-known anatase phase was observed depending on the annealing temperature. The best conditions of crystallization were found to be annealing higher than 400 °C in air. The surface morphology of the deposited films was characterized by the FEG scanning electronic microscopy (FEGSEM). The UV-Vis-NIR spectroscopy shows that the film exhibits a high transmission around 80%. The indirect band gap of the deposited films was found to range between 3.17 and 3.44 eV depending on the annealing temperature.

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PC-55

AT THE ELECTRODE SURFACE. ON THE TURNOVER NUMBER IN ELECTRO-CATALYSIS.

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$RuCl_3(CH_3CN)_3$ is a mediator for the anodic oxidation of several organic compounds, such as tetralin, and cyclohexene. $RuCl_3(CH_3CN)_3$ has two reversible voltammetric waves at 0.15 and 1.85V(in AN, vs. Ag|AgCl|3M KCl) each of a single-electron transfer (SET). A distinct catalytic current appears at 1.85V in presence the mentioned organic compounds. The SET, at 0.15V, remains unaffected and serves as an internal standard [1].

The actual turn-over-number (TON) of a catalyst in such voltammetry experiment depends on a complex of experimental parameters including diffusion control, scan rate, relative concentrations and more. Assessment of TON by voltammetry is therefore not viable.

Using a rotating ring disk electrode (RRDE) the value of "**n**", n= ET per unit of the ruthenium complex at 1.85V is measured in absence and in presence of organic substrate (tetralin). Hence, RRDE provides a straightforward measure of the TON for the catalytic current, (relationship shown on poster). Indeed the TON varies by experimental terms. It is larger at low rotation rates of the RRDE. It depends on the ratio of tetralin to Ru complex. Further proof that the observed currents are a direct measure of **n** is the ratio of ring current to disk current at various rotation rates. The distinct decrease of this ratio at low rotation rates, is explained by shortened supply of Ru^{IV} to the ring and mainly by the longer time available for the *homogeneous* reaction between Ru^{IV} and tetralin to take place on the disc at the expense of Ru^{IV} transfer to the ring.

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PC-56

SYNTHESIS AND CHARACTERIZATION OF GOLD SHELL ARCHITECTURES AND CATALYTIC APPLICATIONS

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Synthesis, characterization, and functionalization of self-assembled, ligand-stabilized gold nanoparticles are studied in the chemistry of nanomaterials. In this work, we synthesized gold clusters, Au_n (n = 25, 39, 55), stabilized of Schiff Base and we studied the catalysis for aerobic oxidation of alcohol.

The gold cluster compounds were characterized by various techniques (UV-vis), (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), X-ray photoelectron (XPS), TEM, AFM and electrochemical characterization for effect of the number of layer.

The studies have shown that a partial electron transfer from the Au anion into the LUMO (π*) to O2 generates superoxide- or peroxide-like species and Lewis acidic centers, both of which play essential roles in the catalytic reactions.

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ELECTROCHEMICAL STUDY ON HOMO/LUMO ENERGIES OF DIPHENYLPYRROLOPYRROLE DERIVATIVES

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Recently, organic pigments are in centre of focus due to their prospects in photovoltaic applications and non-linear optics as well as development of gas sensors. One of the examined chromophores is represented by 3,6-diphenyl-2,5-dihydro-pyrrolo-[3,4-c]-pyrrole-1,4-dione (DPP). Recently, some new derivatives were synthesized and tested for eletronical applications. In this contribution, some derivatives were electrochemically investigated and chraracterized using cyclic voltammetry (CV) and rotating disc voltammetry (RDV) at platinum electrode in non-aqueous media (acetonitrile) in order to estimate the respective reduction and oxidation potentials, to prove the reversibility of these electron transfers and stability of the radical intermediates, to determine electrochemically the HOMO-LUMO gap, to describe the influence of various substituents and to localize the first oxidation and first reduction center (that means the HOMO and LUMO orbitals) on the molecule.

From the CV and RDV experiments resulted that there are two reversible redox processes. In the structure, where two piperidine heterocycles bind to both phenyl goups it has been found that the first oxidation process consumed two electrons (concerted) whereas the derivative with only one piperidine group showed only one-electron oxidation process as well as reduction processes in both derivatives. The oxidation has been also performed by chemical way (with $FeCl_3$) and the result was rather surprising when the oxidation showed to be stepwise. The further experimental data interpretation was focused on influence of N-alkyl or N-ester substitution in pyrrole structure on first oxidation (HOMO) and first reduction (LUMO) processes. Both of the substitutions establish solubility of DPP derivatives in organic solvents. Whereas the length of alkyl chain does not play any important role in electrochemical behavior the ester is saving HOMO-LUMO gap but the shift in redox potentials is evident. The explanation of this manner can be found in rotation of phenyl groups due to the steric effect[1]. Based on these measurements it will be possible to find optimal substituents and thus to "tune" the properties of DPP derivatives for special electronic applications.

Acknowledgements
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PC-58

PREPARATION, CHARACTERIZATION AND LITHIUM INTERCALATION INTO Nb_2O_5 ELECTRODES FOR A RECHARGEABLE LITHIUM BATTERY

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In recent years, great interest has been centered on the development of lithium batteries consisting of lithium intercalation electrodes. Many researchers focus on cathodes which possess a higher voltage vs lithium metal anode because high-voltages cathodes give a higher specific energy density for a given capacity cathode. Several families of materials have studied to meet new cathodic compounds in lithium batteries. Among them is the Li-niobium pentoxide which have interesting energetic and intercalation/de-intercalation properties.

Niobium pentoxide was prepared by decomposition of niobic acid.

The electrochemical lithium intercalation process into the monoclinic pentoxide was examined and compared to the commercial compound which is the good candidate for the cathodic application of lithium metal rechargeable batteries.

The characterization of the oxide products was carried out by X-ray diffractometry (XRD).

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3-D ENSEMBLES OF LINEAR AND BRANCHED ZnO NANOELECTRODES FOR PHOTOELECTROCHEMICAL APPLICATIONS

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ZnO is a wide band-gap semiconductor which is attracting growing attention because of its facile nanostructuration in several forms such as nanoflowers, nanorods, nanoplatelets etc. These unique morphologies and their spatial organization are closely related to enhancement in physico-chemical properties, leading to novel applications in a variety of fields such as photovoltaics[1], biosensors[2], gas sensors, photocatalysis, field emission, piezoelectrics[3]. In heterogeneous processes the increase of the surface area is always an attractive characteristic since, often, high surface area means high reaction rate. Following this viewpoint, in this communication we present a new electrosynthetic way to obtain organized ZnO nanostructures with improved surface area. The main goal is to obtain new nanostructures with improved performances in electrochemical and photocatalytic applications.

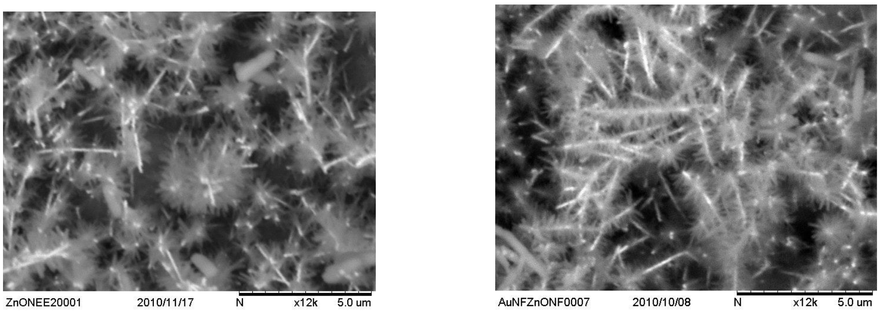

Figure 1a-b. SEM immages of branched

In particular, linear nanofibres of ZnO were obtained by electrochemical growth both on flat ITO electrodes and on 3-D ensembles of metal nanowires[4]. By this way, on the latter substrate, branched hierarchical nanostructures in the shape of nano-pine trees (Figure 1a-b) can be obtained. Linear and branched nanofibres have been characterized by FE-SEM (field emission scanning electron microscopy), EBSD (electron backscattered diffraction) and electrochemical methods. The photochemical properties of these electrodes were tested with respect to the photodegradation of some water pollutants.

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STRUCTURAL PROPERTIES OF TRIMETALLIC ACETILYDE COMPLEX $[(Ru(CO)_2(\eta^5\text{-}C_5H_5))_3(\eta^2\text{-}C_2)]$

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Transition metal complexes containing acetylide ligands were first reported almost 30 years ago, and since then they have remained an area of active research in organometallic chemistry. The π system of the linear C≡C group provides a pathway for delocalization of electron density between the metal and ligand and, hence, an efficient mechanism for communication between two or more metal centers. Polymeric metal acetylides may, therefore, have potential applications in nonlinear optics , where extensive mixing of ligand- and metal-based orbitals is necessary for a large nonlinear response , in the development of conducting materials , and also in artificial light harvesting chromophores . The reaction of the silver complexes $[\{\{Ru(CO)_2(\eta\text{-}C_5H_4R)\}2(\eta^1{:}\eta^2\text{-}C{\equiv}C)\}_3Ag_3][BF_4]_3$ (R = H or Me) with $[RuCl\text{-}(CO)_2(\eta\text{-}C_5H_4R)]$ at room temperature gave the new trimetallic complexes $[\{Ru(CO)2(\eta\text{-}C_5H_4R)\}_3(\eta^1{:}\eta^2\text{-}C{\equiv}C))][BF_4]$ which contain the acetylide ligand surrounded by ruthenium atoms.

Density functional calculations accurately reproduce the structures of ours compound $[(Ru(CO)_2(\eta^1\text{-}C_5H_5))_3(\eta^2\text{-}C_2)]^{+1}$, and provide new insights into the its properties, Moreover, An orbital molecule analysis, establish the relative importance of various orbital in bonding and suggest possible week interaction between the atomic orbital of Ru and the acetilyde moieties. This result also supports the bonding nature of Ru-C bonds suggests by Mayer's bond order calculation.

Keywords: Density functional calculations, trimetallic acetilyde complex

CHEMICAL SYNTHESIS OF HIGH SPECIFIC AREA NANOSTRUCTURED MNO$_2$ POWDERS IN VIEW OF THEIR USE AS ACTIVE MATERIALS IN BATTERIES AND SUPERCAPACITORS

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Manganese dioxides are promising active materials because of their high specific energy, low toxicity, and low cost. The synthesis of sea urchin like nanostructured MnO_2 powders was successfully realised by a chemical method with two different oxidizing agents. The characterization by SEM, EDX, and TEM techniques confirms the nanometric structure of these powders. The X-ray diffraction technique shows that the obtained crystallographic variety is γ-MnO_2, often considered as the most reactive form.

The electrochemical reactivity of these powders was investigated in 1 M KOH by cyclic voltammetry and electrochemical impedance spectroscopy by using a cavity microelectrode. The results reveal that the MnO_2 synthesized with $Na_2S_2O_8$ shows the highest electrochemical reactivity in the test medium. This is due to its crystallographic variety γ-MnO_2 which is largely used as cathodic material for primary batteries.

Another promising approach concerns the use of these powders as active materials in supercapacitors. Preliminary results show that the capacitance of an active mixture formed from nanostructured MnO_2 powders and industrial PICA is better than that of industrial PICA.

Acknowledgements

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PC-62

ON-LINE MASS SPECTROMETRY INVESTIGATION OF THE CO_2 ELECTROREDUCTION IN ACIDIC MEDIA ON FE/C CATALYSTS.

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During the last years, CO_2 concentration in the atmosphere has been increasing, being the major responsible of global warming. Therefore, reducing CO_2 emissions has become a critical issue. Different methods have been developed to reduce its emissions. Among them, the electrochemical route allows the consumption of CO_2 at the same time that obtaining useful chemical products (1). However, it is necessary to develop new catalysts to increase the activity and selectivity of the process. With this purpose, in this work Fe catalysts supported on Vulcan XC-72R have been prepared by the polyol method using ethylenglycol as solvent and reducing agent. Prior to the metal deposition, Vulcan was subjected to different oxidation treatments, using HNO_3 or a HNO_3-H_2SO_4 1:1 (v/v) mixture, in order to create functional groups. This will allows the study of the influence of the surface chemistry of the support on the properties of the catalysts. Comparison with Pt/Vulcan material has been performed also.

Supports were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), temperature programmed desorption (TPD), N_2-physisorption and thermogravimetric analysis. During the oxidation treatments, oxygen surface groups were created, being the most severe treatment the most effective. On the other hand, the specific surface area and the resistance to air oxidation of the materials decreased indicating a partial destruction of the original morphology.

Catalysts were characterized by energy dispersive X-ray analysis (EDX), XRD, SEM and N_2-physisorption. Results showed that Fe was dispersedly deposited along the carbon materials. However, it was not possible to determinate the metal crystallite size by XRD as characteristic diffraction peaks of Fe were not observed suggesting that the metal was deposited on the supports with amorphous structure and/or with a metal crystallite size inferior to 2 nm. The electrochemical properties of the catalysts were studied in 0.5 M H_2SO_4, at room temperature and atmospheric pressure by cyclic voltammetry and chronoamperommetry. Simultaneously, the formation of gaseous and volatile products during the reduction of CO_2 was followed “in situ” by differential electrochemical mass spectrosmetry (DEMS). Results showed that for Pt electrode the H_2 evolution is favoured but not the formation of CO_2 reduction products. On the other hand, the functionalization of carbon Vulcan with concentrated HNO_3 decreased the activity of Fe catalysts in the CO_2 reduction reaction. However, when the support was treated with HNO_3-H_2SO_4, the activity towards the formation of carbon-hydrogenated products increased, making more interesting the CO_2 reutilization process.

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PC-63

NANOSTRUCTURED PROTON CONDUCTIVE MEMBRANES BASED ON SULFONIC ACID INTERPENETRATING POLYMER NETWORKS

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Fuel Cells (FC) development, for both stationary and mobile applications, is pointed as a key issue in the energy scenario of the next two decades. Particularly, in PEMFC (Proton Exchange Membrane FC or Polymer Electrolyte Membrane FC), the optimization of proton conductive membranes and the search for new membranes has gained crescent attention over the last decade (1). Among the strategies for obtaining proton conductive membranes with enhanced characteristics, the development of interpenetrating polymer networks (IPN) may present advantages concerning mechanical and chemical stability. These properties, if combined with high proton conductivity, may allow the application of these IPN as membranes in efficient PEMFC devices (2). The present work describes the characterization of sulfonated IPN membranes based on the diglicidyl ether of bisphenol A (DGEBA) and polyethyleneimine (PEI).

IPN membranes containing 38 and 41 %wt PEI (IPN_{38} and IPN_{41}, respectively) were obtained from solution polymerization, using standard procedures. The sulfonic acid membranes ($IPN\text{-}SO_3H$) were obtained directly from the IPN membranes, based on a procedure adapted from Rocco and co-workers (3). Aiming to evaluate the efficiency of the polymerization and sulfonation reactions, FTIR spectra were collected and analyzed, evidencing the formation of a reticulated polymer network and the presence of sulfonic acid groups covalently bonded to aromatic rings. In addition, vibrational spectra evidenced the presence of protonated ($–SO_3H$) and dissociated ($–SO_3^-$) acid forms, indicating an equilibrium between these forms: $IPN–SO_3H + n\ H_2O \rightleftharpoons IPN–SO_3^-(H_2O)_{n-1}(H_3O^+)$.

Electrochemical impedance spectra of the $IPN–SO_3H$ membranes were collected under 100% relative humidity at temperatures between 20 and 80 ^oC, from which the conductivity (σ) values were found, in the range between 10^{-4} and $10^{-3}\ \Omega^{-1}cm^{-1}$. The apparent activation energy (E_a) values indicated a predominantly vehicular proton conduction mechanism and maximum conductivity of $5.21\times10^{-3}\ \Omega^{-1}cm^{-1}$ was obtained for the $IPN_{41}–SO_3H$ membrane, at 80 ^oC. Proton conductivity values in this order of magnitude are often found for polymer gels, highly hydrated systems or membranes with higher mobility, containing ionic liquids and aprotic solvents (4). In the present work, the nanostructure of the obtained IPN, combined to their hydrophilic behavior, allows the high conductivity values achieved and the water retention up to high temperatures.

CNPq, FAPERJ, Rede $ProH_2$/MCT ProPPi/UFF

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ELECTROCHEMICAL CHARACTERIZATION OF A 11-MERCAPTOUNDECANOIC SELF-ASSEMBLED MONOLAYER COVALENTLY COUPLED WITH PYRIDOXAMINE.

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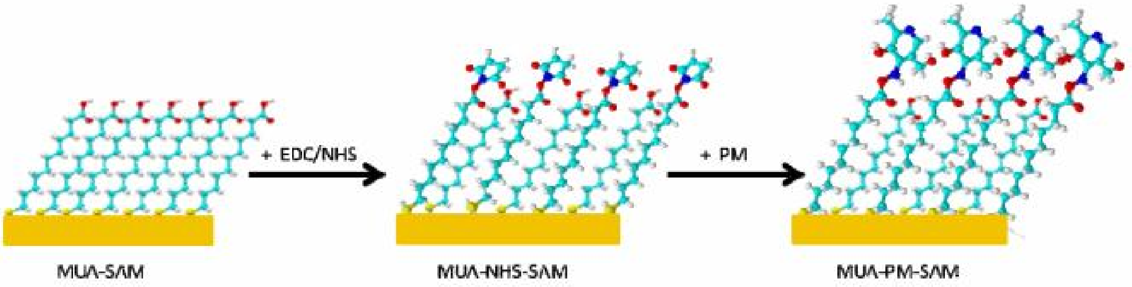
Alkanethiol functionalized self-assembled monolayers (SAMs) are commonly used to covalently immobilize biorecognition molecules on surfaces. The specific molecular structure of the SAMs can be appropriately chosen to control the orientation, distribution and spacing of the sensing element. The SAM can be tailored to present a hydrophobic or charged surface. A general procedure for covalent immobilization of molecules onto carboxy-terminated alkanethiol SAMs involves the formation of an amide bond by first producing a hydroxysuccinimide ester (NHS) that is displaced by the amine derivative.



Scheme 1

In this work we present the electrochemical characterization of a SAM bearing pyridoxamine (PM) molecules. To obtain this derivatized monolayer, we have first constructed a SAM of 11-mercaptoundecanoic acid (MUA) onto a Au(111) single crystal electrode by immersing it in a solution 1 mM MUA for 24 h. The covalent activation was started by firstly contacting the rinsed MUA-SAM electrode with a solution of EDC/NHS for 1 h and secondly with a solution of PM (Scheme 1). The modified electrode was characterized by studying the reductive desorption process after each step of the SAM formation. The results agree with an increase of the layer stability, as demonstrated by lowering the potential for the reductive desorption, upon attaching NHS and PM molecules on the SAM external surface. Moreover, the electrochemical response of $K_3Fe(CN)_6$ redox probe has been also studied. The presence of the MUA layer totally inhibits the ferrocyanide redox signal.[1] Upon modification of the MUA layer, the degree of inhibition of the redox response is dependent on the chemical nature of the layer.

Acknowledgments: Project CTQ2010-16137, Junta de Andalucía (FQM 111) and Universidad de Córdoba.

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TiO_2 NANOSTRUCTURED POROUS ELECTRODES: A WAY TOWARD TIME-RESOLVED SPECTRO-ELECTROCHEMISTRY

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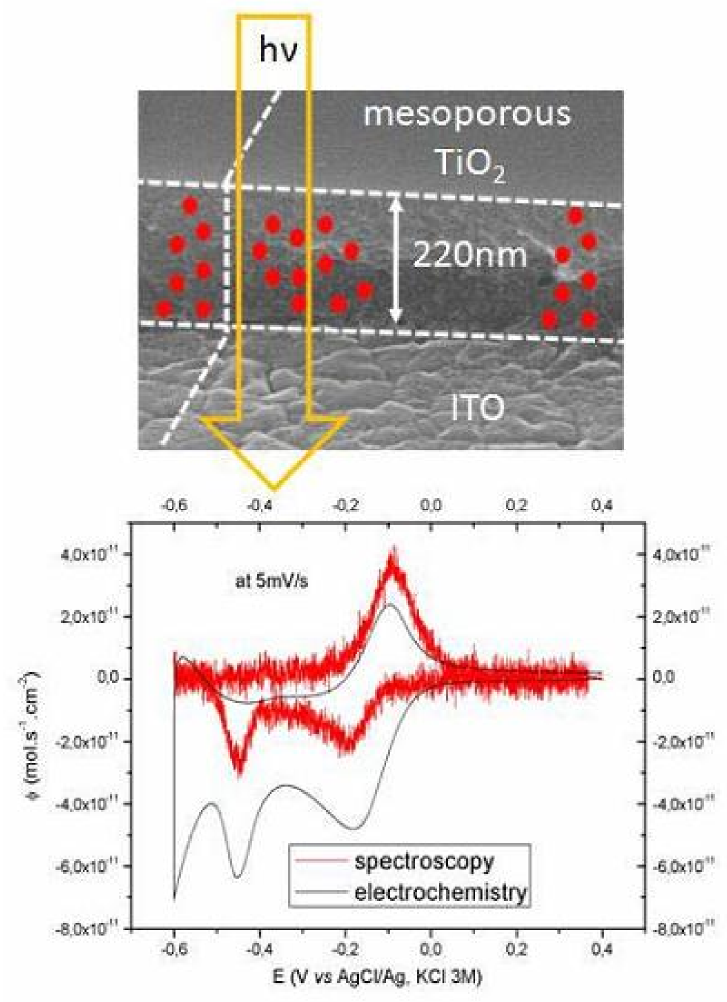

Recent progresses in material synthesis allow the deposition of transparent well ordered mesoporous conducting oxide films. They present a great interest for bioelectronic devices based on the immobilization of redox active biomolecules. Using a sol-gel method (E.I.S.A.), a mesoporous dioxide titania film (1) of c.a. 220 nm thickness was deposited on conducting glass substrat to achieve time-resolved spectro-electrochemical characterization of redox protein. Results obtained with immobilization of porphyrins and protein will be shown. Taking advantage of the simultaneous measurement of UV-Visible absorbance spectra and current, conduction in this mesoporous semi-conducting structure was detailed and direct electron transfer with a non denatured protein was observed.

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PC-66

BIMETALLIC PtSn NANOCATALYSTS SUPPORTED ON ZEOLITE/CARBON COMPOSITES.

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Polymer Electrolyte Fuel Cells (PEMFC) have their cost strongly influenced by the use of Pt as nanoelectrocatalyst. Alternatives for overcome this issue involve the use of other metals along with Pt, thus forming bi- or trimetallic catalysts, and the replacement of catalyst supports, typically, Vulcan Carbon XC-72, by other nanostructured materials. Bi- and trimetallic catalysts containing PtRu and PtSn have proved to be suitable for application in direct ethanol cells [1] however; most of PtSn catalysts, even if prepared by different methods, show no alloying behavior. Our group has studied the use of a ZSM-5:Carbon (50:50 wt%) composite as catalyst support, using a method adapted from Pang and co-workers [2]. The main goal of the present work is to obtain PtSn catalysts supported onto these ZSM-5:Carbon composites, and their characterization by X-ray diffraction (XRD) and cyclic voltammetry (CV) in aqueous H_2SO_4 0.5 M.

PtSn/ZSM-5/C samples were prepared utilizing a Pt:Sn atomic ratio of 1:1, keeping the Pt content 10 and 15 %wt of the support. The XRD analyses showed diffraction peaks between 20 and 25^o attributed to the (002) plane of the carbon hexagonal phase and also the Pt face centered cubic structure (fcc) characteristic peaks, at $2\theta = 39.7$; 46.2; 67. 7 and 81.9^o, related to the (111), (200), (220) and (311) diffractions, respectively. These peaks are shifted to slightly smaller angles (2θ) than those found for pure Pt catalysts, suggesting the occurrence of a lattice expansion due to the presence of Sn atoms. This lattice expansion indicates the formation of a PtSn alloy phase, observed by other authors on the study of such bimetallic catalysts, however, supported on Vulcan Carbon XC-72 [3]. The peaks at $2\theta =$ 55.2 and 62.4° are present for all samples and are attributed to ZSM-5, as well as other peaks with $2\theta < 37^o$.

By using the Scherrer equation, average particle sizes of 3.88 and 5.80 nm were calculated for samples containing 15 and 10 %wt Pt, respectively. The lattice parameters found were 0.3940 and 0.3926 nm, respectively, higher than the value 0.3916 nm calculated for a commercial sample containing 20 wt% Pt over Vulcan XC-72R (Electrochem). Analyses of the cyclic voltammetry of the PtSn/ZSM-5/C nanocatalyst containing 10 %wt Pt showed electrochemical active area (EAA) of 18.8 m^2/g.

The preparation of the PtSn/ZSM-5/C nanocatalysts were observed along with the formation of a bimetallic alloy phase, and samples containing 10 %wt Pt exhibited higher EAA than PtSn obtained on carbon with higher Pt concentration.

CNPq, FAPERJ, Rede ProH_2/MCT

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ELECTROCHEMILUMINESCENCE NANOPHOTONIC SENSOR INSTRUMENT FOR DETECTION OF DANGEROUS BACTERIUM IN SURROUNDING WATER AND BIOLOGICAL LIQUIDS

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Microorganisms include bacteria, viruses, fungi, viroids, prions and parasites. One of the unique representatives of microorganisms are bacteria. They are widely spread in nature, for instance, bacteria inhabit soil, water, human organism and animals, plants etc.

The water is a native habitat of various microorganisms including bacteria. In its coastal zone (lakes, seas etc.), especially near a big population center, the water contains large quantity of a strange bacteria, including pathogenic and opportunistic pathogenic one. Many foodstuffs (milk, meat, fish, eggs, fruits, vegetables and etc.) are favorable environment for bacteria reproduction. The fundamentals of bacteria pathogenicity are their property to form of toxins, which may be detected by variety of analytical methods [1].

We live in an era of technological revolutions that continue to impact our lives. So development of new modern and efficient methods of dangerous bacteria early detection is quite urgent task. For its successful solution different types of sensors using nanomaterials including spherical semiconductor quantum-dimensional structures (SQDS) as detection elements can be developed. In a lot of recently published articles SQDS technologies for biosensing applications are described. SQDS are bright and photostable materials with broad excitation spectra. Furthermore, their emission spectra are tunable in a wide range from UV to NIR due to the quantum size effect. Various modified with different compounds water-soluble SQDS having good biocompatibility and low cellular toxicity have been synthesized and their different applications were discussed [2, 3].

In this paper a novel method of ecotoxicants detection based on SQDS as detector elements of nanophotonic sensor instrument and electrochemiluminescent intensity as analytical signal is considered. For development of proposed assay method and sensor possible bacterial toxin and analytes molecule structure and energy were calculated; electrochemical and electrochemiluminescent properties of SQDS were investigated. Selected SQDS were plotted on sensor working electrode by Langmuir-Blodgett method. The detection limit and assay procedure selectivity were obtained.

The work was supported by Science and Technology Center in Ukraine projects ##4495 and 5067 (Project manager Prof. Mykola Rozhitskii).

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REDOX-ACTIVE NANOPARTICLES: SYNTHESIS AND ELECTROCHEMICAL BEHAVIOR OF VIOLOGEN MODIFIED STÖBER SILICA PARTICLES WITH A DIAMETER OF 125 nm

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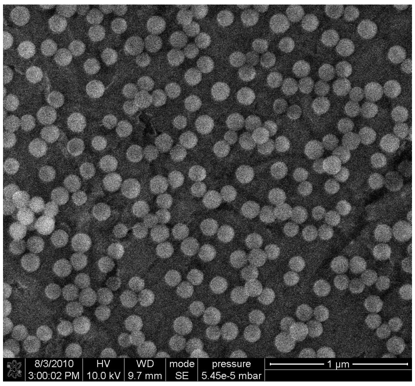
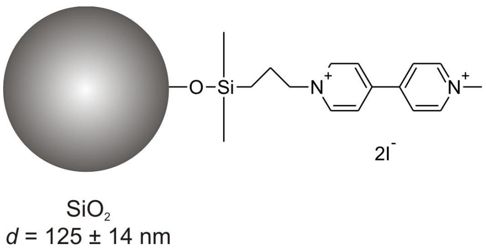
Non-porous *Stöber* silica nanoparticles(1-3) with a diameter of approximately 125 nm and low polydispersity have been synthesized and characterized by means of DRIFT, SEM, DLS, BET as well as density (Gay-Lussac pycnometry) measurements. The hydroxy-terminated particles were modified with an alkoxy-substituted viologen salt through a condensation reaction in dimethylformamide. CP/MAS NMR and DRIFT spectra indicate the successful immobilization of the viologen derivative.





In solution, the hexafluorophosphate salt of the alkoxy-substituted viologen shows two reduction processes(4) that are coupled to adsorption effects(5) when applying high negative potentials. The modified material spontaneously adsorbs at Pt electrodes with hydrophilic surfaces and can therefore be studied by cyclic voltammetric experiments. The electrochemical behavior of the redox-active particles in non-aqueous electrolytes is compared to the free viologen modifier with respect to the observed reduction potentials.

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CATALYTIC OXYGEN REDUCTION BY SELF ASSEMBLED WATER SOLUBLE COBALT PORPHYRINS AT A LIQUID|LIQUID INTERFACE

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The 4-electron reduction of molecular oxygen (O_2) in aqueous media is a challenge in the development of fuel cells and batteries. Current efforts have been focused in the development of new electrocatalysts. In particular, cobalt porphyrins exhibit good activity for the reduction of oxygen, although the principal product is H_2O_2 (2-electron reduction). Nevertheless, cofacial porphyrins dimers can carry out the 4-electron reduction. However, in nature, the oxygen reduction occurs at biomembranes, *i.e.* soft interfaces which allow the charge separation process. The interface between two immiscible electrolyte solutions (ITIES) can be considered as a bioinspired system useful to study fundamental processes of biocatalysis.[1,2]

In this work, we study the oxygen reduction at a water|1,2-dichloroethane interface using tetrathiafulvalen (TTF) as sacrificial donor (in the organic phase) and catalyzed by water soluble ($CoTMPyP^{4+}$ or $CoTPPS^{4-}$). A common ion in both phases was used to polarize the interface positively in order to pump protons from the aqueous to the organic phase. The catalytic activity was estimated following the formation of the radical cation of TTF, and the quantity of produce H_2O_2 was followed by UV-visible absorption after titration of the aqueous phase with sodium iodide.

Afterwards, the formation of a dimer between the two porphyrins was investigated by UV-visible absorption spectroscopy, and it was also used as catalyst. A highest activity and a better selectivity towards H_2O were observed in this case.

Surface second harmonic generation (SSHG) analyses were also carried out. These experiments can explain the differences between the activities of the three catalysts investigated, since the reaction is expected to happen mostly at the interface.

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SPOTTING-BASED FUNCTIONALIZATION OF OPTICAL NANOTIP ARRAY FOR MULTIPLEX MOLECULAR BIOSENSING

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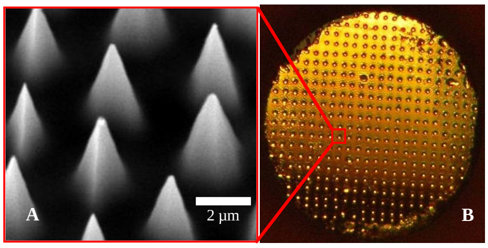
We have developed a DNA nanosensor array on an original optical support. A coherent bundle of 6,000 optical fibers is transformed in an ordered array of nanoelectrodes which are then functionalized by electrocopolymerization of a thin polypyrrole film including oligonucleotide (ODN) probes. The fabrication of the nanoelectrode array has already been detailed elsewhere.(1) To obtain a multiplexed biochip, an electrochemical cantilever has been used to deliver very small amount of solution (2). The spots are realized by electrocopolymerization of pyrrole and pyrrole-ODN monomers (3) in the limit of the picoliter drop on the conductive surface. The same process is repeated with other probe-containing solutions at determined positions of the plateform, and so different probes have been addressed onto the same nanoelectrode array (4). It allows to obtain high-density DNA chips which are able to perform remote fluorescence imaging with the advantages of ultramicroelectrode properties. Since such nanostructured optical surfaces are efficient SERS substrates (5), this approach could lead to new label-free plasmonic biosensors.



A) SEM image of the functionalized optical nanotips. B) Image of ~400 spots deposited on nanostructured electrode (D).

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PC-71

THIANTHRENE-BASED BRANCHED SEGMENTS AS FIELD-EFFECT MOBILITY MATERIALS

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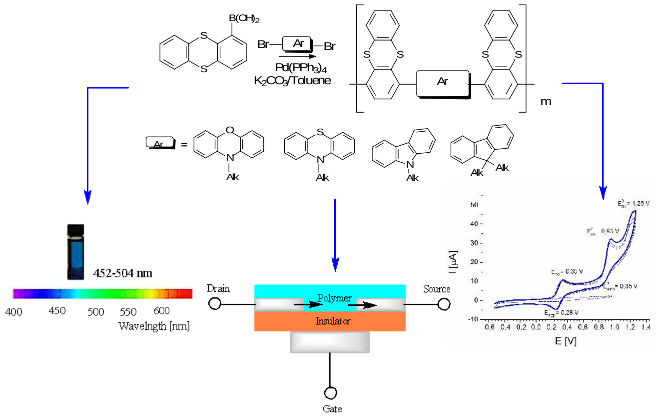
Conducting polymers have widespread industrial applications owing to a unique combination of mechanical, optical, and electronic properties. One of its promising application is in the area of chemical and biological sensors [1]. While high selectivity can be achieved by tuning or modifying the chemical and physical properties of conducting material, high sensitivity can be obtained by operating them as field-effect transistors (FETs) because of the ability of FETs to amplify *in-situ* and to gate-modulate channel conductance [2]. Field-effect mobility is a widely used benchmark for the electrical transport performance of organic semi-conductors. Its magnitude is an important characteristic of an organic material because it defines its capability to carry current [3]. Incorporation of thianthrene with π-donor properties to conducting polymer backbone is one an expected central organic unit for the construction of new type of donor with redox properties, resulting copolymers possessed high electron affinity and preferential charge-transporting properties.

In these contents, we report series of symmetric thianthrene based materials bearing a phenoxazine [4], phenothiazine, carbazole and fluorene as a functional segments. The new oligo(arylene)molecular structures were obtained by palladium-catalyzed Suzuki-cross-coupling methodology, one of the most efficient tool in now days organic synthesis. We report also the photophysical properties and the moieties of the thin films built of monomers and polymers and their electrochemical character (Scheme).



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NEUTRAL METAL BIS(1,2-DITHIOLENE) COMPLEXES : MOLECULAR MATERIALS FOR ORGANIC ELECTRONIC APPLICATIONS

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This work is part of a project funded by the ANR dedicated to the design of new molecule architecture for organic photovoltaic cells.

The synthesis of new electron acceptor materials combining several properties: thermal stability and stability in air, strong absorption in near infrared and infrared spectral domain is presented.

We decided to work on neutral nickel bisdithiolene complexes because they are known to be very stable in air and temperature until 300 °C and they absorb strongly between 750 nm to 1100 nm. Thus, their use in photovoltaic cells for infrared part of the sun light is of great interest. Several series of complexes have been synthesized with dpedt (diphenyl-ethylenedithiolate) ligands [1]. Their physicochemical behaviors were characterized by using different techniques among them cyclic voltammetry and square wave voltammetry [2].

The results show that they all have high electron affinity. In particular, it is shown that the HOMO-LUMO energy gap of such complexes can be modulated as a function of functional groups grafted on the dpedt ligands. All these properties make these compounds very interesting for photovoltaic application.

Keywords: coordination chemistry, organic chemistry, molecular materials, organic photovoltaics, metal bisdithiolenes, liquid crystal, near infrared dye.

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FIRST STAGES OF GROWTH OF NANOPOROUS OXIDES ON TITANIUM IN ORGANIC FLUORIDE-CONTAINING ELECTROLYTE

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Nanostructured oxides on titanium metal have been extensively investigated due to the variety of applications including sensors, photocatalysis, solar cells and biomedicine (1,2). This is particularly related to their valuable chemical and physical properties, including mechanical and thermal resistance, low electrical conductivity, chemical inertness, permeability, and biocompatibility. Anodic oxidation has proven to be a promising route to the fabrication of nanotube arrays of different shape, pore size, length, and wall thickness by varying anodization parameters such as the applied voltage, fluoride and water content. One of the best results so far were obtained in ethylene glycol (EG)-based electrolytes with the addition of fluoride and small amounts of water(3)).

In the present paper, an investigation of the initial stages of barrier film growth and dissolution on Ti in EG/H_2O electrolyte with 0.015-0.20 M NH_4F using electrochemical and surface analytical techniques is reported. Steady-state current-potential curves and electrochemical impedance spectra as depending on potential in the range -0.1/5.0 V vs. AgCl/Ag reference electrode were registered. In addition, chemical composition of the oxides formed at 0.1 to 1.5 V in electrolytes containing 0.06 and 0.20 M NH_4F were estimated by X-ray photoelectron spectroscopy (XPS).

Preliminary treatment of the impedance spectra allowed for the estimation of the barrier layer thickness and ion migration rate coefficient as depending on applied potential and fluoride content of the electrolyte. XPS analysis revealed the presence of a non-stoichiometric oxide containing mainly Ti^{4+} and a certain amount of Ti^{3+}, with a significant degree of hydroxylation. Estimates of the total thickness of the oxide from the XPS data using a dual layer model are also presented. On the overall, the effect of added fluoride leads to higher current densities and higher film thicknesses at constant potential, which is in overall accordance with the findings of previous authors for thick nanoporous oxides (4). A kinetic model of the process to quantitatively interpret the electrochemical and surface analytical results based on the surface charge approach is currently being elaborated.

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VOLTAMMETRIC RESPONSE OF MWCNT-FE OBTAINED BY AC ARC DISCHARGE METHOD

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Cyclic voltammetry is used to study electrochemical behavior of working electrode modified with MWCNT-Fe (multiwall carbon nanotubes with Fe nanoparticle embedded in their structure). The multiwall carbon nanotubes were prepared by AC arc discharge method. For this study, the voltammograms were recorded for different concentrations of H_2SO_4 and different scanning speeds. Results from cyclic voltammetry demonstrated that the MWCNT-Fe have significant electrochemical activity due to their special structure.

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PREPARATION AND CHARACTERIZATION OF BITHIOPHENE MODIFIED Si(1,1,1) ELECTRODES

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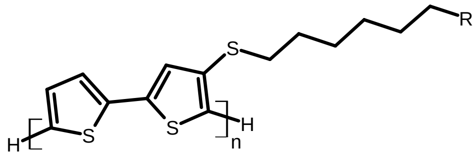
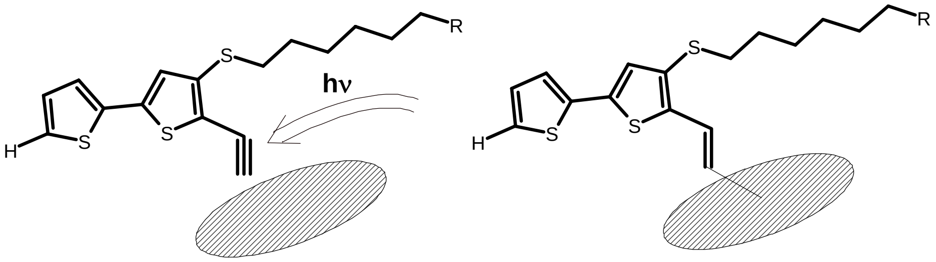
The purpose of this work is to prepare a substituted oligothiophene (OT) (*Figure 1*) modified electrode[1], in which the oligomer is capable of acting as a conductive wire between the electrode surface and the solution bulk.



R = CH_3, CN, COOH

Fig.1: The oligothiophenes

A simple model system is represented by a bithiophene chemically grafted to the surface of an hydrogen terminated n-doped Si(111) electrode. The grafting is achieved by UV triggered addiction of an alkyne moiety *via* a double bond formation (*figure 2*).



R = CH_3, CN

Fig. 2: The BT grafted to the silica surface

The organic film was characterized with various techniques, such as Cyclic Voltammetry, MALDI-TOF, XPS.
The presence of the double bond allows to extend the conjugation (and thus the conductivity) of the OT chain to the electrode (transducer).
The possibility to functionalize with different moieties the lateral chain and the thiophene rings makes these system very versatile and easily customizable.

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SURFACE PATTERNING WITH ARYL BASED FILMS BY APPLICATION OF SCANNING ELECTROCHEMICAL MICROSCOPY (SECM)

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It is well established that aryl radicals exhibits high reactivity towards a large variety of materials, ranging from carbon-based substrates over metals to semiconductors, resulting in chemisorbed films spanning from monolayer to multilayers. These radicals are often formed by electrochemical reduction of the corresponding aryldiazonium salt.[1] Another route to establish thin organic films on electrode surfaces is by anodic oxidation of arylhydrazines in basic aqueous solution, where the oxidation potential was observed to be strongly dependent on the solution pH value. The process is believed to go through a three-electron process, in which the arylhydrazine is oxidized to the aryl radical, the grafting agent, via an intermediate formation of the corresponding aryldiazene. In this work, the scanning electrochemical microscope is used to generate a local increase in pH, which enables the local modification of a surface with an organic film in the micrometer range. Experiments were compared to simulations in order to achieve more insight into the grafting mechanism.

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PC-77

PROTON-COUPLED ELECTRON TRANSFER (PCET) IN TRANSITION METAL PORPHYRINS BEARING 2,6-DI-*TERT*-BUTYLPHENOL PENDANTS

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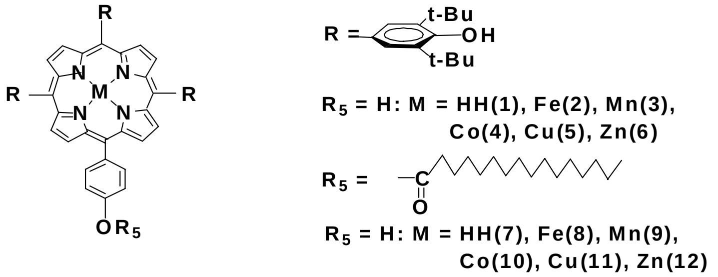
Proton-coupled electron transfer (PCET) reactions play a critical role in a wide range of biological processes including photosynthesis and respiration as well as in the activation of small molecules involved in conversion and storage of solar energy [1]. In previous studies the possibility of PCET in ferrocene derivatives with 2,6-di-*tert*-butylphenol moieties was demonstrated [2].



The novel transition metal porphyrins **9-20** with 2,6-di-*tert*-butylphenol pendants were synthesized and their redox properties have been studied by CVA, EPR, UV-vis spectroscopy and kinetic measurements .The electrochemical data demonstrate the possibility of the intramolecular proton-coupled electron transfer (PCET) as a result of ligand’s redox-state change.

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CONJUGATED SYSTEMS ALTERNATING BENZENE/THIOPHENE CONDENSED RINGS: EFFECTIVE CONJUGATION AND ELECTROCHEMISTRY

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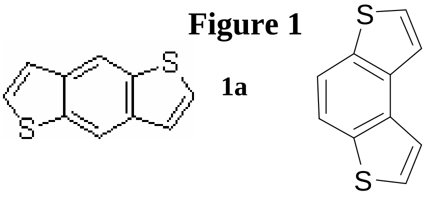
Thiophene-based oligomers are a boundless class of organic semiconductors and starting materials for the preparation of electroactive films with attractive functional properties for energy, optoelectronic and sensor applications. Starting from the parent model series of linear α-oligothiophenes, of high planarity and high conjugation efficiency but low solubility, many structure modifications have been developed so far, aiming to improve solubility and processability (*e.g.* by inserting alkyl chain substituents or adopting branched structures), to tune HOMO and LUMO energies and localization on the conjugated system (*e. g.* by inductive effects of appropriate substituents) and to enhance 3D properties, including chirality (*e. g.* purposedly inserting distorsions along the main conjugated backbone). The effective conjugation of the main conjugated backbone is a key parameter in determining the electronic properties of these molecular materials, such as their HOMO-LUMO energy gaps, which regularly decrease with increasing effective conjugation. Effective conjugation depends on the *nature*, the *number*, and the *connectivity* of the aromatic rings constituting the π-conjugated system.

We are currently investigating by electrochemical techniques the case of conjugated systems consisting of alternating condensed benzene and thiophene rings(1), resulting in higher conjugation with respect to both all-benzene and all-thiophene condensed systems, and having free α terminal thiophene positions.

In this context, we will discuss the effect of *ring connectivity* contrasting the electrochemical behaviour of two benzodithiophene isomers (Figure 1), accounting for different planarity and different HOMO and LUMO energies and gaps; further tuning of HOMO and/or LUMO, in terms of both position and energy, can be achieved by adding convenient substituents on either the aromatic and/or the heteroaromatic rings.

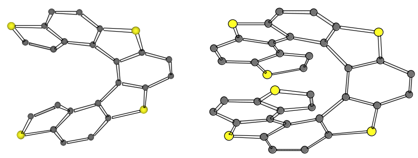
Figure 1



1a

1b

Furthermore, in the case of parent molecule 1b, *increasing the number of condensed rings* results in helicoidal bending (for $n_{ring} \geq 4$) affording the thiahelicene series, hinging on a helix-like conducting backbone with attractive 3D features and intramolecular π-stacking effects.



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INTERCALATION - SORPTION PROPERTIES OF SUPERCAPACITOR HIGH CAPACITY ELECTRODES BASED ON NANOSTRUCTURAL CARBONS

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In the framework of high specific energy electrochemical capacitors elaboration, the electrodes based on nanostructural activated carbons (powder ADG and carbon-clothes CH900 and TSA) with specific surface area 1000 -1500 m^2/g in concentrated solution of sulphuric acid (30%-60% mass fraction) at the wide voltage range (from -1V to +1V) have been studied. The cycle volt-ampere curves measured at two voltage ranges have been compared. These voltage ranges can be named as a reversible range (from 0.1V to 0.9V) and a deep charging range (от -0.8V до 1V). The first one corresponds to the charging of electric double layer and fast redox-reaction of surface groups in approximately 1-100s time. Here total specific charge is about 200 C/g. As for the second one, in the range of negative potential (< -0.1 B) the faraday processes with extremely high pseudo capacity values and charging time from hundreds of seconds to tens of hours are observed. At these times, not only above mentioned fast processes proceed. Taking into account obtained results, it can be assumed that there are also the processes of chemical hydrogen adsorption on interfacial area carbon/electrolyte and the electrochemical hydrogen intercalation in carbon at deep cathode charging of activate carbons take place. The intercalation process is governed by slowed solid-phase hydrogen diffusion, which may explain very high maximal time of charging until 100 hours as well as the proportionality peak current to square root from the potential scan rate. The fact of limiting charge growth with increasing of sulphuric acid concentration (from to 30% to 60%) has been established and the maximal total charge of 1560 C/g has been obtained. Impedance spectroscopy researches of activated carbons electrodes and separately resistance measuring of these electrodes at direct current have been made. The essential increase (in ten times) of electrodes resistance at deep cathode charging process has been found. It may be due to formation of intercalated C_6H, analogous one is C_6Li. The specific charge increase with increasing concentration of sulphuric acid. As is known, the intercalation of sulphuric acid in graphite or in similar to graphite material takes place. Expansion of space between graphen layers is growing, where the acid can penetrate. As a result it can be supposed that in our case the double intercalation takes place. Sulphuric acid intercalates in activated carbons and increases interlayer space between graphen layers. Then the atoms of hydrogen come to this space at deep cathode charging. Consequently the interlayer space works as transport way for hydrogen, which interacts with graphen layers and forms compound C_6H in the limit.

A two-dimensional mathematical model of carbon electrode charge-discharge process has been developed. The model takes into account the following factors: charging of electric double layer, adsorption of hydrogen at an interface carbon/electrolyte, electrochemical hydrogen intercalation into carbon, solid-diffusion, diffusion-migration ion transport in the pores, the characteristics of the electrode porous structure measured by using the method of standard contact porosimetry [1].

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HETEROGENEOUS PHOTOCATALYSTS PREPARED BY ELECTRODEPOSITION OF TIO_2 ON PT-NANOPARTICLES

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Heterogeneus photocatalysis occurs when the surface of a semiconductor oxide is irradiated with photons with at least band-gap energy (E_{bg}). The electrons in the valence band (VB) are excited into the conduction band (CB), creating holes in the first. Both holes and electrons have to reach the semiconductor surface in order to catalyze reduction and oxidation processes of suitable compounds in the electrolyte solution. The application of this process to photosplitting of water and solar energy conversion has been widely studied, in particular for TiO_2 [1]. However, the quantum yields achieved so far have been far from optimal caused by electron-hole recombination [2].

In this work, the development of new materials aiming on addressing specifically the problem of recombination is demonstrated. The prepared materials were designed to using reproducible and low cost electrochemical methods. The selective deposition of different amounts of TiO_2 by means of electrochemically induced methods on Pt nanoparticles on FTO and ITO has been studied. These obtained composite samples were evaluated with respect to their potential of being used as electrodes for the production of hydrogen by photoelectrochemical water splitting. The results obtained so far show that the amount of TiO_2 deposited on the Pt nanoparticles does not have an effect on the photocurrent of the surfaces, when irradiated with UV light.

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DEVELOPMENT AND ELECTROCHEMICAL CHARACTERISATION OF A BIOSENSOR BASED ON SEMICONDUCTING SILICON STRUCTURES TRANSDUCTION

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Impedance spectroscopy is a rapidly developing electrochemical technique for the characterization of biomaterial–functionalized electrodes and biocatalytic transformations on the electrodes surface, and specifically for the transduction of biosensing events at electrodes. Such technique has been used in our work as a tool for the characterization of a new nitrite biosensor for environmental applications based on the immobilization of catalase on insulator-semiconductor (IS) systems (p-Si/SiO_2/Si_3N_4).

The principle of the developed biosensor includes the following: Catalase catalyzed the breakdown of H_2O_2 into H_2O and O_2. Nitrite was selected as an inhibitor of catalase. Under optimal conditions, i.e. buffer capacity corresponding to 3 mM phosphate buffer, the catalase enzyme insulator semiconductor sensors shows a high sensitivity to nitrite detection. In both cases, the responses of these biosensors based on nitrite additions are good with the detection limit around 10^{-11} M. It is expected that such an original and promising concept of inhibitor-based biosensors based on reactivation by inhibitive effects, will be useful for the development of environmental smart biosensors based on the integration of ENFET with the corresponding instrumentation in the same silicon chip.

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PC-82

PREDICTION DE NOUVEAUX CATALYSEURS BIMETALLIQUES SOLIDES PAR LA TECHNIQUE DU DATAMINING

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Le choix raisonnable des catalyseurs solides pour la synthèse de divers composés minérale et organique à faible couts est un défi pour les décennies avenirs. Bien que les approches empiriques sont très utilisées dans la fabrication des catalyseurs, les méthodes de modélisations telles que le calcul du premier principe, doivent être explorées et développées [1-3].

On présente une nouvelle approche basée sur le datamining, pour la conception de nouveaux matériaux à usage industriels comme catalyseurs hétérogènes plus performant et ceci en utilisant les propriétés structurale, thermodynamique et élastiques de nouveaux alliages de métaux de transitions et des autres métaux du tableau périodiques peu exploités. L'analyse en composantes principales (ACP) [4-6] et la régression aux moindres carrés partiels (PLS) [7], des techniques d'informatique, ont été appliquées pour prédire de nouveaux matériaux.

Les tendances de la dureté et la ductilité de ces matériaux sont identifiés à l'aide de critères physiques et empiriques, et validés avec les observations expérimentales. Le rapport B/G de module du cisaillement (G) et de compressibilité (B) sont utilisés pour évaluer les comportements : fragilité / ductilité des alliages des métaux de transitions.

L'application de ces tendances à la sélection de matériaux afin de concevoir des catalyseurs plus performants démontre que cette approche peut être utilisée, non seulement pour interpréter les observations expérimentales existantes, mais elle pourrait aussi être utilisée pour prédire de nouveaux matériaux avec les propriétés désirées.

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PERFORMANCES OF THE GEL-POLYMER ELECTROLYTES BASED ON POLYESTER DIACRYLATE

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The problem of developing of polymer electrolytes for lithium-polymer batteries is problem of today. Due to the growth of hybrid cars and electric vehicles production there are of increasing requirements for its safety. Replacing of the liquid electrolyte to the polymer electrolyte enables to solve the above problem.

Thereupon it is a particular interest to the net polymer electrolyte with fully amorphous structure. We have proposed a polymeric electrolytes based on polyester diacrylate (PEDA), which forms a three-dimensional network by radical polymerization.

Under modification of the polymer electrolytes based on PEDA and $LiClO_4$ by the addition of ethylene carbonate (EC) the extremal dependence of the ionic conductivity on the EC concentration was obtained. To understand of these features was fulfilled a comprehensive experimental and theoretical study using IR spectroscopy and quantum chemical modeling. We found that the experimental IR spectra changed by steps at increasing of EC content. Finally the same absorption peaks as observed in IR spectra for solutions of $LiClO_4$ in EC are formed. The study by density functional theory of the structure of mixed complexes of Li^+ with EC and the PEDA, which was modeled by oligomers $H-((CH_2)_2COO(CH_2)_2O)_n-CH_3$, $n \leq 4$, showed that at low EC content (1-2 molecules per ion Li^+) mixed complexes with one molecule of EC are formed. It provokes stronger binding of lithium ion with the polymer matrix and leads to a decrease in conductivity. With an increase of EC proportion, the Li^+ ion presumably forms solvate complex with 4 EC-ligands and polymer electrolyte conductivity achieve the value of 2×10^{-4} S/cm at 20ºC and 1×10^{-3} S/cm at 100ºC.

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