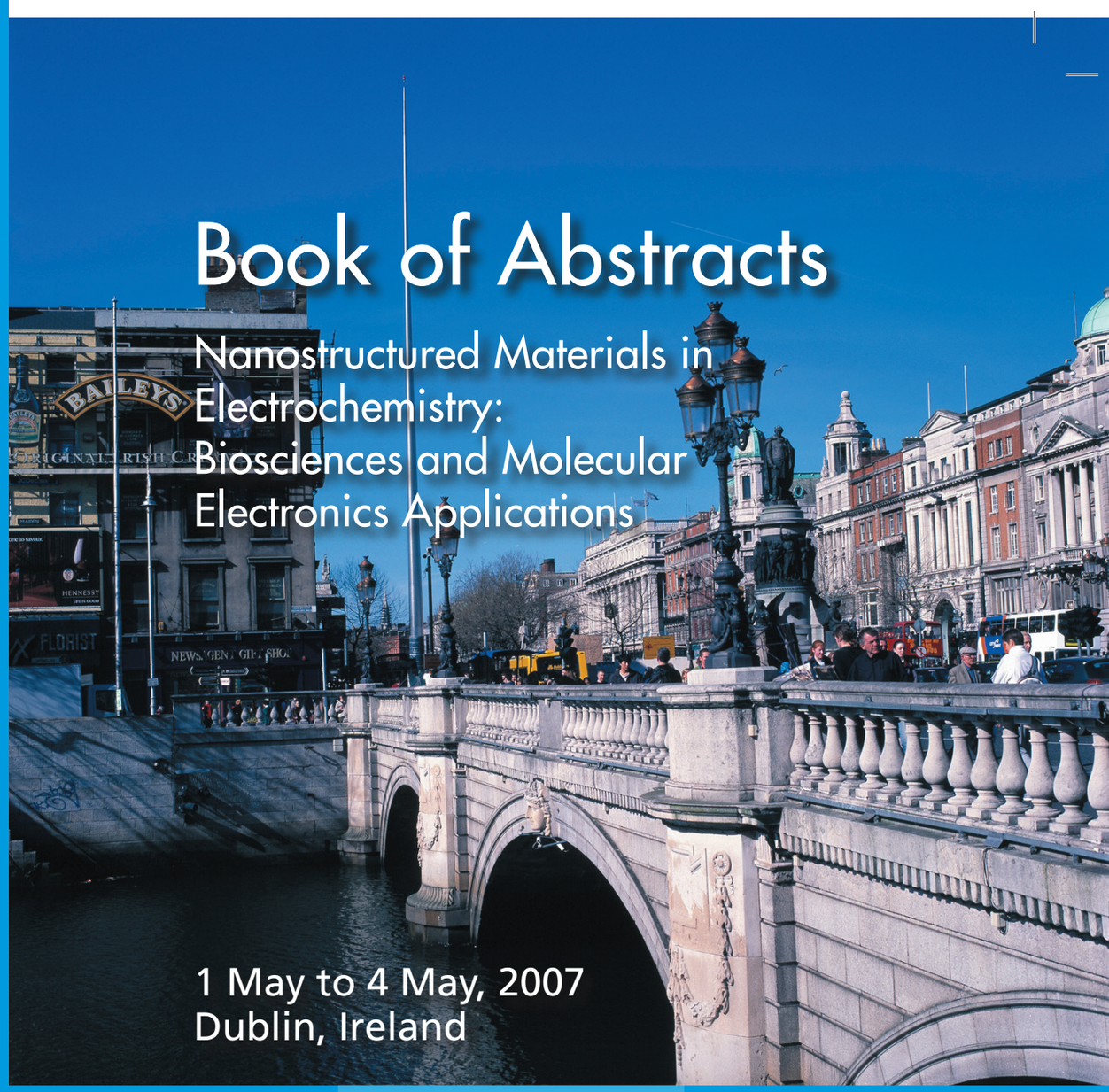
Book of Abstracts – 5th Spring Meeting of the International Society of Electrochemistry



Book of Abstracts

Nanostructured Materials in Electrochemistry: Biosciences and Molecular Electronics Applications

1 May to 4 May, 2007
Dublin, Ireland

5th Spring Meeting

of the International Society of Electrochemistry

Book of Abstracts of the

5th Spring Meeting of the International Society of Electrochemistry

Nanostructured Materials in Electrochemistry;
Biosciences and Molecular Electronics Applications

Book of Abstracts of the

5th Spring Meeting of the International Society of Electrochemistry

Nanostructured Materials in Electrochemistry;
Biosciences and
Molecular Electronics Applications

Dublin, Ireland
1 – 4 May, 2007

International Society of Elecrtochemistry
Avenue Vinet 19
1004 Lausanne
Switzerland

Printed in The Netherlands

Organising Committee

Chairman
Tim McCormac, *Ireland*

Robert Forster, *Ireland*
Lo Gorton, *Sweden*
Ole Hammerich, *Denmark*
Marcin Opallo, *Poland*
Wolfgang Schuhmann, *Germany*

Local Organising Committee

John Cassidy, *Dublin Institute of Technology*
Eithne Dempsey, *Institute of Technology Tallaght Dublin*
Robert Forster, *Dublin City University*
Mike Lyons, *Trinity College Dublin*
Edmond Magner, *University of Limerick*

Acknowledgements

Sponsors and Exhibitors


Agilent Technologies

Centre for Research In Electroanalytical Technology

DiagnoSwiss


Failte Ireland

IJ Cambria Scientific Ltd


Institute of Chemistry of Ireland

Institute of Technology Tallaght

Ivium Technologies

JPK Technologies


Materials and Surface Science Institute
Centre for Spectroscopy

Nuclear Centre for Sensor Research

Nuclear Magnetic Resonance Institute

Science Foundation Ireland

The Electrochemical Society


Uniscan Instruments


Windsor Scientific/Ecochemie

Table of Contents

Invited Lectures

Oral Presentations

Table of Contents

Poster Presentations

Invited Lectures

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

Heechang Ye and Richard M. Crooks*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712-0165

**crooks@cm.utexas.edu*

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

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

Ralph G. Nuzzo*

Department of Chemistry, The University of Illinois at Urbana-Champaign, Champaign, IL 61801

* r-nuzzo@uiuc.edu

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

Engineering SERS Substrates for Bioelectrochemical Studies

Philip N. Bartlett*,
School of chemistry, University of Southampton, Southampton, SO17 1BJ, UK
**pnb@soton.ac.uk*

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

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

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

References

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

Invited Lectures

Nanoparticles on surfaces for proteomic analysis

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

1: Laboratoire d'Electrochimie Physique et Analytique, Station 6, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

2: Department of Chemistry and Institute of Biomedical Sciences, Fudan Univeristy, Shanghai 200433, P.R. China

**Bhliu@Fudan.edu.cn, Hubert.Girault@epfl.ch*

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

In chip protein digestion : Laser photoablated microchannels are coated with gold nanoparticles and poly(diallyldimethylammonium chloride). This surface is then used to immobilise trypsin The maximum proteolytic rate of the adsorbed trypsin was 400 mM/(min·μg), much faster than that in bulk solution due to the biocompatible microenvironment provided by the gold nanoparticles. The controlled amount of adsorbed trypsin was studied on the basis of the Langmuir isotherm, and the fitted Γ_{max} and K values were estimated to be 1.2×10^{-7} mol·m^{-2} and 4.1×10^{5} M^{-1}, respectively. Trace amounts of standard protein samples down to 16 fmol were confidently digested using the enzymatic microreactor and resulting tryptic products were identified by MALDI-TOF MS/MS.

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

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

Single-molecule "Transistors" from Au-nanoparticles to Proteins and DNA in Electrochemical Environment

J. Ulstrup
Department of Chemistry, Building 207, DTU, DK-2800 Lyngby, Denmark

Scanning tunnelling microscopy (STM) to molecular resolution in *aqueous solution* under substrate and tip double potential control (*in situ* STM) is established and has recently been extended in our group to ionic liquid media. *In situ* STM extends beyond imaging, and offers *two* kinds of tunnelling "spectroscopy", the tunnelling current/*bias* voltage relation at constant electrochemical *overpotential*, and the tunnelling current/*overpotential* relation at constant *bias voltage*. These are equivalent to the current/bias and current/gate voltage relations of molecular transistors. In contrast to reported cases of single-molecule transistors, *in situ* STM-based molecular transistor function operates at *room temperature* in *condensed matter* environment. The accessibility of a chemical *redox centre* in the molecule is crucial in this respect.
In situ STM-tunnelling spectroscopy with "on-off" ratios up to two orders of magnitude is established in our group, with transition metal complexes and a redox metalloprotein (*Pseudomonas aeruginosa* azurin) as prime targets. New results apply to Coulomb blockade effects in Au-nanoparticles (1.6 nm) and to redox-marked oligonucleotides. These quite different systems display molecular electronic amplification features that, however, differ in details of the physical mechanisms. Some perspectives of this will be noted.