



18th Australian Electrochemistry Symposium

Electrochemistry Division – Royal Australian Chemical Institute

Curtin University

Resources and Chemistry Precinct

Bentley, WA

15th April 2012.



Programme
and
Book of Abstracts



Dear Delegates,

You are all very welcome to the 18th Australian Electrochemistry Symposium. The meeting is a forum for the presentation and discussion of research on all aspects of electrochemistry. Together with a programme of contributed lectures and posters, the meeting provides a forum to honour the Electrochemistry Division's 2012 medal winner. These are:

B. Breyer Medallist: Prof. Joseph Wang (UCSD, USA);

R.H. Stokes Medallist: Prof. Justin Gooding (UNSW);

A.M. Bond Medallist: Dr. Jie Zhang (Monash).

As most of you will be aware, this one-day symposium immediately precedes the 10th Thematic Meeting of the International Society of Electrochemistry (ISE) which takes place at the University Club of Western Australia 15-19 April 2012. We thus have the prospect of an amazing few days of electrochemistry here in Perth.

The organising committee thanks everyone who has helped out in putting together this event and especially our sponsors (listed on the following pages), without whom we could not have proceeded.

Organising committee

Damien Arrigan (Curtin University), **Debbie Silvester** (Curtin University), **Conor Hogan** (La Trobe University), **Anthony O'Mullane** (RMIT University), **Chuan Zhao** (University of New South Wales), **Paul Duckworth** (eDAQ Pty Ltd).

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The organising committee thanks the following organisations for their sponsorship of this event:

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Dear Colleague,

I am delighted that you are taking part in an ISE-sponsored meeting and have the opportunity to benefit from interactions with a number of ISE members and the Society. Besides sponsoring scientific meetings of interest to the electrochemical community, the ISE organizes its own Annual and Topical Meetings, publishes its journal *Electrochimica Acta*, and offers ISE prizes to promising young researchers and distinguished scientists.

We are pleased to invite you to become a member of the International Society of Electrochemistry.

There are many reasons for joining the International Society of Electrochemistry. ISE members can obtain:

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- reduced registration fees for ISE Meetings;
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- access to the full membership directory which contains the addresses of all ISE members; and
- support from the Millennium Fund and Presidential Fund for ISE-related scientific activities.

Furthermore, young scientists may apply for the *Electrochimica Acta* Travel Award for Young Electrochemists and ISE Travel Award for Young Electrochemists to attend the ISE Annual Meeting.

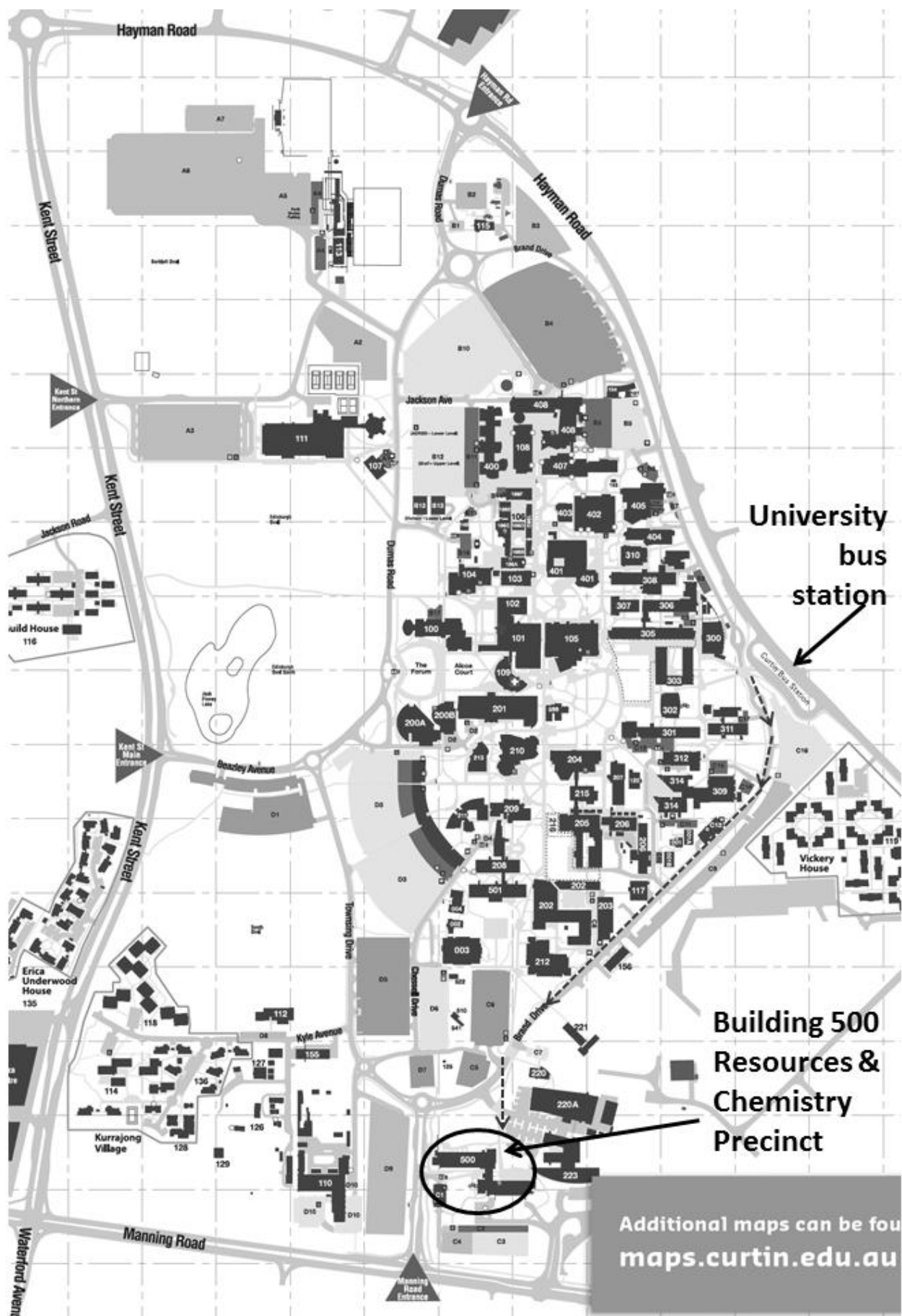
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All you have to do is fill in the Membership Application Form that you can find in the Society web site, at the address: http://members.ise-online.org/members/new_members.php and submit it online. Should you have difficulties in finding two sponsoring ISE members, please write to the Executive Secretary of the Society Dr. M. Musiani, e-mail: m.musiani@ieni.cnr.it. The membership fee for the calendar year 2012 is 40 Euro (10 Euro for age below 30). Once your application is accepted, the ISE Office will contact you for the payment of the membership dues.

Sincerely,

Prof. Mark E. Orszag
President of ISE



LECTURE PROGRAMME

- 8.00 Registration
- 8.30 Welcome
- 8.40 *Breyer Medal* presentation and lecture: **Joseph Wang** (UCSD, USA): Motion-based Biosensing
- 9.25 **Blake Plowman** (RMIT): Templated Electrodeposition of Gold and Platinum Nanostructures For Electrocatalytic Applications
- 9.40 **Kongfa Chen** (Curtin): Degradation and Delamination of (La,Sr)MnO₃ Based Oxygen Electrodes of Solid Oxide Electrolysis Cells
- 9.55 **Xunyu Lu** (UNSW): Tuning the Ionic Liquid Electrolytes Toward Efficient Electrolysis of Water
- 10.10 break
- 10.40 *Bond Medal* presentation and lecture: **Jie Zhang** (Monash): Proton Coupled Electron Transfer Reactions in Ionic Liquids
- 11.10 **Stefan Klink** (Bochum, Germany): Tailoring of CNT Surface Oxygen Groups by Gas-Phase Oxidation and Its Implications for Lithium Ion Batteries
- 11.25 **Omar Abdul-Rahim** (Monash): Generation and Stabilisation of Stilbene Dianion with Ionic Liquids or TCNQ
- 11.40 **David Williams** (Auckland, NZ): Electrochemical Switching of Polymer Brushes Grafted Onto Conducting Polymer Films
- 11.55 **Abbas Barfidokht** (UNSW): Regain of Electrochemistry on Passivated Electrodes Decorated by Gold Nanoparticles: Thickness Dependence of the Passivating Layer
- 12.10 words on behalf of some of our sponsors.
- 12.15 lunch and posters
- 13.30 **Alan Bond** (Monash): Extraction of metal ions from aqueous solutions with methimazole-based ionic liquids
- 13.50 **Susana Cordoba de Torresi** (Sao Paulo, Brazil): Electro-controlled swelling of a full polymeric 3-D conducting monolithic device
- 14.05 **Manzar Sohail** (USC): A New Ion-to-Electron Transducer for Solid-State Polymeric Ion Sensors Based on Ferrocene Tagged Polyvinyl Chloride
- 14.20 **Jacqui Delaney** (La Trobe): Use of Mobile Cell Phone for the Generation and Detection of Electrogenenerated Chemiluminescence in Low Cost Sensors
- 14.35 **Eva Alvarez de Eulate** (Curtin): Adsorptive stripping voltammetry of lysozyme via adsorption-desorption at liquid|liquid microinterfaces
- 14.50 break
- 15.15 **Alan O’Riordan** (Tyndall, Ireland): Discrete Gold Nanowire Arrays: An Electrochemical Study
- 15.30 **Leigh Aldous** (UNSW): Towards the Electrochemical Quantification of the Strength of Garlic
- 15.45 *Stokes Medal* presentation and lecture: **Justin Gooding** (UNSW): Dispersible Electrodes: Gold Coated Magnetic Nanoparticles for Electrochemical Sensing
- 16.20 Finish
- 16.30 for delegates of the ISE meeting: coach-facilitated transfer to the ISE meeting registration/reception at University Club of Western Australia.

POSTER PROGRAMME

Poster No.	Presenter(s)	Affiliation	Poster Title
P1	Moinul Choudhury	University of New South Wales	Electroactive Monolayers on n-Type Silicons
P2	Masniza Sairi Binti & Salmah Abdul Aziz	Curtin University	Chronoamperometric study of ion transfer at nano- and micro-ITIES arrays
P3	Xin Chen	University of New South Wales	Detection of Trace Nitroaromatic Isomers Using AgNPs/ β -Cyclodextrin Modified ITO Electrodes
P4	Shane O'Sullivan	Curtin University	Electrochemical behaviour of proteins at arrays of liquid-liquid microinterfaces
P5	Roland de Marco	University of the Sunshine Coast	Electrochemistry at the Liquid-Liquid Interface of a Droplet of Water and 1,2-Dichloroethane
P6	Amit Bansiwai	National Environmental Engineering Research Institute, India	Arsenic Detection using Functionalised Metal Nanoparticle Modified Screen Printed Electrodes
P7	Stephen Parker	University of New South Wales	Capture and Releasing Rare Circulating Tumour Cells Using Electrochemically-Switchable Surfaces
P8	Junqiao Lee	Curtin University	A Langmuir Trough study of the interactions between syndiotactic-PMMA and ISE-dopants probed by neutron/x-ray reflectometry
P9	Elizabeth Murago	University of New South Wales	Towards a Multiple-Analyte Sensor by use of Dispersible Modified Au@Fe ₃ O ₄ Nanoelectrodes
P10	Thomas Somerville	Macquarie University	Enhanced electron transfer at a glassy carbon electrode modified by covalently attached graphene oxide
P11	San Ping Jiang	Curtin University	Electrochemically Induced Electrode/Electrolyte Interfaces of Solid Oxide Fuel Cells
P12	Bryan Suryanto	University of New South Wales	Exploitation of Protic Ionic Liquids as Electrolytes for Electrodeposition of Metals
P13	David Bower	La Trobe University	Low cost LEECs based on room temperature ionic liquids
P14	Paul Clayton	MEP Instruments	A modified concentration variable for facile standard addition calculations using Excel spreadsheets, together with a simplified estimation of relative uncertainty for analyte determinations
P15	Krish Murugappan	Curtin University	Screen-Printed Electrodes for Ammonia Gas Sensing in Ionic Liquids

P16	Roya Tavalai	University of New South Wales	Surface Modification of Gold Coated Magnetic Nanoparticles via Electrografting of In Situ Generated Aryl Diazonium Cations
P17	Manika Mahajan	RMIT University	Facile synthesis of TCNQ based organic charge-transfer complexes with photocatalytic and catalytic applications
P18	Roberto Torresi	Universidade de São Paulo, Brazil	The influence of water content on the physicochemical and electrochemical properties of ionic liquids
P19	Chris Gunawan	University of New South Wales	Controlled Electrocrystallization of Metals from Protic Ionic Liquids
P20	Vickramjeet Singh	Guru Nanak Dev University, India	Volumetric Interactions of Some Saccharides in Aqueous Solutions of Sodium Gluconate and Their Role in Taste Behavior
P21	Na Ai	Curtin University	Performance and stability of Pd infiltrated YSZ oxygen electrodes of solid oxide electrolysis cells
P22	Pauline Michaels	University of New South Wales	Characterisation of DNA modified Si(111) and Si(100) using Electrochemical Impedance Spectroscopy
P23	Ellen Reid	La Trobe University	New Electrochemiluminescent Horizons: Novel Platinum Schiff-base Complexes
P24	Ilija Najdovski	RMIT University	Rapid electrochemical synthesis of highly active Cu/Pd and Cu/Au bimetallic honeycomb films
P25	Aravind Ramachandran	University of New South Wales	Modified Electrodes for Detecting Bacterial Activity
P26	Egan Doeven	La Trobe University	New Dimensions in Electrochemiluminescence
P27	Alexander Weremfo	University of New South Wales	Characterization of Electrochemically Roughened Platinum Electrode: Exposure to the Atmosphere
P28	Varun Rai	Nanyang Technological University, Singapore	Electrochemical DNA Sensor for Ultrasensitive DNA Sequence Specific Detection of Legionella sp. and Dengue
P29	Chee-Seng Toh	Nanyang Technological University, Singapore	Self-Powering Amperometric Sensor and Biosensor
P30	Corie Horwood	University of Calgary, Canada	Effect of anodization conditions on the formation of low-aspect-ratio tantalum oxide nanotubes
P31	Qi Li	Monash University	Electrochemically Directed Synthesis and Properties of Structurally Characterized [TTF] ₄ [SVM11O ₄] (M = Mo, W; TTF = tetrathiafulvalene) Charge Transfer Materials

1. Medal Award lecture abstracts.

Motion-based Biosensing

Joseph Wang

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The remarkable performance of biomotors is inspiring scientists to create synthetic nanomachines that mimic the function of these amazing natural systems (1). Particular attention will be given to catalytic nanowire and microtube motors propelled by the electrocatalytic decomposition of a chemical fuel, as well as to fuel-free (magnetically or electrically-driven) nanomotors.

This presentation will describe new motion-based bioassays based on changes in the speed or distance of nanomotors induced by biomolecular interactions or on the selective capture, sorting and transport of target biomolecules (2). Different motion transduction schemes will be illustrated for monitoring a wide range of biomolecular interactions of nucleic acids, proteins or cancer cells. Key factors governing such motion-based sensing will be discussed. The resulting assays add new and rich dimensions of analytical information and offer remarkable sensitivity, coupled with simplicity, speed and low costs. We will discuss the challenges of implementing molecular recognition into the nanomotor movement and for generating well-defined distance signals. Microengines functionalized with different receptors will be shown to capture selectively and transporting target DNA and cancer cells from raw body fluids. The greatly improved capabilities of chemically-powered artificial nanomotors could pave the way to exciting and important bioanalytical applications and to sophisticated nanoscale devices performing complex tasks.

References:

1. "Can Man-Made Nanomachines Compete with Nature Biomotors?" J. Wang, *ACS Nano*, 3(2009)4.
2. "Motion-based Sensing and Biosensing using Electrochemically-Propelled Nanomotors", S. Campuzano, D. Kagan, J. Orozco, J. Wang, *Analyst*, 136(2011)4621.

Dispersible Electrodes: Gold Coated Magnetic Nanoparticles for Electrochemical Sensing

J. Justin Gooding¹, Leo M.H. Lai¹, Ian, Y. Goon², Kyloon Chuah¹, Elizabeth Murago¹, May Lim², Rose Amal²

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Nanoparticles have attracted enormous interest in biosensing related to a range of unique properties they possess. Here we will present our findings on using gold coated magnetic nanoparticles as dispersible electrodes that can be sent out into the sample, collect the analyte and bring it back to an macroelectrode for detection. This strategy is shown to give highly sensitive sensors that have much faster response times than classical macroscopic sensors. Here how the particles are made [1] is discussed followed by how they perform as electrodes before demonstrating their surface modification strategies to convert these nanoparticles into selective nanoelectrodes for sensing [2]. Applications of these dispersible nanoelectrodes are demonstrated for the sensing of metal ions [3], proteins such as prostate specific antigen, and small organic molecules such as the antibiotic enrofloxacin. These three examples all demonstrate different transducing formats in which these dispersible electrodes can be employed, from straight amperometric detection, to labelling approaches and finally employing these particles in biochemresistors.

Acknowledgements

We would like to thank the Australian Research Council and the University of New South Wales for funding this research

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Proton Coupled Electron Transfer Reactions in Ionic Liquids

Jie Zhang, Shu-Feng Zhao and Alan M. Bond

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Currently, many researchers are actively working in the area of carbon dioxide (CO₂) fixation due to the need for new energy sources and the negative environmental impact of CO₂ as a major green house gas. Ionic liquids have attracted considerable attention in this application since they exhibit many desirable properties for this application, such as: (1) high CO₂ solubility; In fact, many ionic liquids have been used for CO₂ capture; (2) high electrochemical stability; (3) high conductivity and (4) low volatility; in addition to other widely recognized properties. Unfortunately, breakthroughs are few despite active research. Our studies suggest that very often the desired products could not be obtained in ionic liquids, or could be obtained but with very low yield, compared to those obtained in conventional organic solvent media. Further mechanistic studies reveal that this and other unexpected experimental observations could be attributed to the proton availability of ionic liquids, even though ionic liquids are widely accepted as media with high chemical stability.

In this talk, I will present the findings of our ongoing project on the electrochemical conversion of CO₂ in ionic liquids. This talk consists of three parts: (1) the remarkable effect of proton availability on the electroreduction of benzophenone; (2) a unique proton coupled electron transfer pathway for electrochemical reduction of acetophenone in ionic liquid [BMIM][BF₄] under a CO₂ atmosphere; and (3) the voltammetry of adhered microparticles as a convenient method to access “water free” reversible potentials for water sensitive reduction of benzophenone and 1,4-benzoquinone in “wet” (water content ~ 0.13 M) 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Bmpyr₄][NTf₂]) ionic liquid.

2. Contributed lecture programme abstracts.

Templated Electrodeposition of Gold and Platinum Nanostructures For Electrocatalytic Applications

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The synthesis of novel nanostructured materials is an area attracting much attention due to their interesting properties and wide range of applications.[1] This extends to the field of electrochemistry, where such materials commonly show enhanced behaviour compared to their bulk form and are therefore being explored in areas such as electrocatalysis and electroanalysis. In this work, the synthesis of novel metallic nanostructures through chemically templated electrodeposition techniques is explored, resulting in the formation of materials such as gold nanospikes[2, 3] (Fig. 1a) and hierarchical platinum-lead nanostructures (Fig. 1b). This facile method of synthesis forms nanostructured surfaces with a good degree of adhesion and homogeneity. Of particular note is the absence of lead in the gold nanospike surface while in the case of electrodeposited platinum the formation of a Pt-Pb bimetallic surface occurs which is known to be beneficial in certain applications.[4] The mechanism of formation and enhanced electrocatalytic activity of these materials towards important reactions such as glucose, methanol and formic acid oxidation is investigated, which also significantly demonstrate greater tolerance to poisoning than their bulk counterparts.

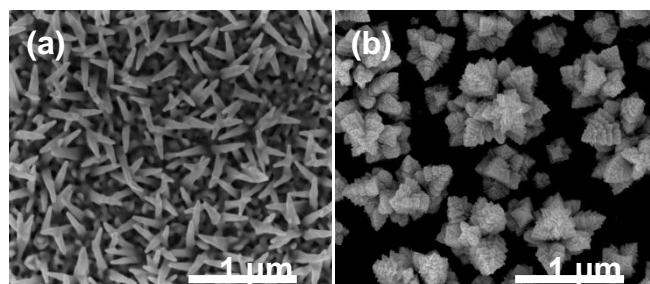


Figure 1. SEM images of gold nanospikes (a) and hierarchical platinum-lead nanostructures (b) formed through the use of chemical templating.

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Degradation and Delamination of (La,Sr)MnO₃ Based Oxygen Electrodes of Solid Oxide Electrolysis Cells

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High temperature solid oxide electrolysis cells (SOECs) are highly efficient for hydrogen and syngas production [1]. However, one of the major problems for the long-term stability of SOEC stacks is the degradation of the common used (La,Sr)MnO₃ (LSM) oxygen electrodes [2]. In this presentation, a detailed fundamental study on the degradation of both the pure LSM and LSM-Y₂O₃-ZrO₂ (YSZ) oxygen electrodes under the SOECs operation conditions will be presented. The results show that the incorporation of YSZ not only significantly enhances the electrochemical activity of LSM, but also substantially affects the electrode behaviors during the anodic operation (Fig. 1a). The anodic current passage primarily affects the low frequency electrode process firstly, while the high frequency electrode process as well as the ohmic resistance is significantly deteriorated in the final stage (Fig. 1b). The low frequency process is enhanced for the pure LSM electrode, but is deteriorated for the LSM-YSZ electrode. The LSM particles at the electrode/electrolyte interface of both the electrodes are broken up into nanoparticles by the SOEC operation, leading to the delamination and failure of the electrodes. The nanoparticles formation, however, has different effects on the low frequency electrode process of the LSM and LSM-YSZ electrodes. It is suggested that enhanced reaction area on the LSM surface and a high proportion of ion conducting phase in contact with the electrolyte are essential for highly performing and good stability of LSM-based electrodes.

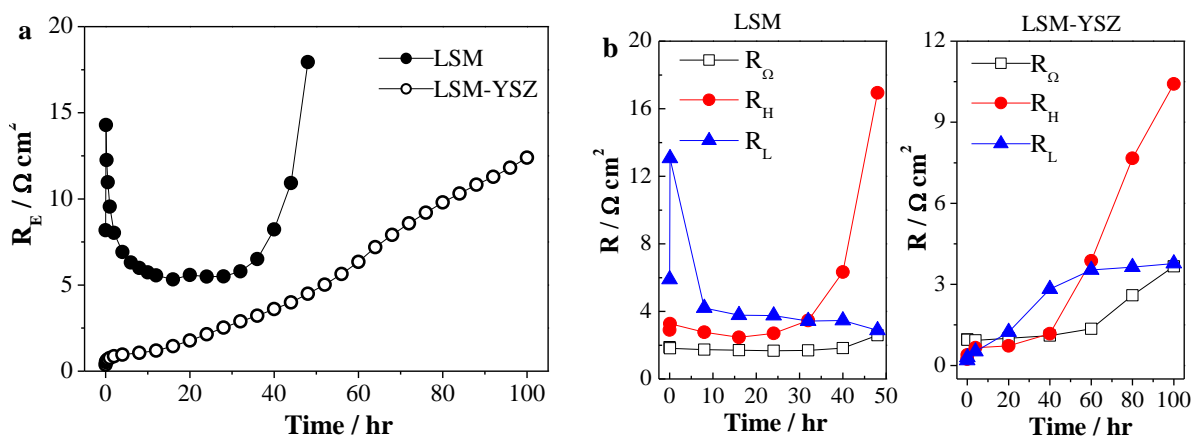


Fig. 1. (a) Overall electrode polarization resistance (R_E) and (b) plots of the electrode ohmic resistance (R_Ω), electrode polarization resistances associated with high and low frequency impedance arcs (R_H and R_L) for the reaction on a LSM and a LSM-YSZ electrodes as a function of anodic current passage time at 500 mA cm⁻² and 800°C.

References

- [1] Z. Zhan, W. Kobsiriphat, J.R. Wilson, M. Pillai, I. Kim, S.A. Barnett, Energy & Fuels, 23 (2009) 3089.
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Tuning the Ionic Liquid Electrolytes Toward Efficient Electrolysis of Water

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The design of efficient systems for splitting water into hydrogen and oxygen, driven by sunlight and other types of renewable energy sources, is among the most important challenges facing science today, underpinning the long term potential of hydrogen as a clean, sustainable fuel. Most research in water splitting so far has been materials-based. Few have looked into the effects of electrolytic environment on efficiency. The vast majority of electrolytes used so far in water splitting still represent conventional inorganic acids or salts such as H_2SO_4 , Na_2SO_4 and KOH .

In this study, a series of novel protic ionic liquids (PILs) have been prepared. The electrochemical properties of these PILs, including potential window, internal potential reference, double layer capacitance as well as steady state response, were characterized. Some of these PILs have wide electrochemical potential window, together with high conductivity and low viscosity, is capable to be used as an electrolyte for electrolysis of water. The as prepared PILs as well as two classic aprotic ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfate (BMIM-triflate) and 1-ethyl-3-methylimidazolium trifluoromethanesulfate: (EMIM-triflate) have been applied as electrolytes for electrolysis of water, and very high faradaic efficiency of these ILs electrolytes have been obtained. The stability of these three ILs electrolytes were tested by cyclic voltammogram (CV) and a range of spectroscopic techniques such as ^{13}C NMR. Importantly, our results show that the oxidation overpotential of water is strongly dependent on the electrolytes used, and lower overpotential for water oxidation can be achieved by using ionic liquid electrolytes than conventional inorganic electrolytes such as Na_2SO_4 . This has opened a new pathway to enhance water splitting efficiency by tuning the electrolytes.

Tailoring of CNT Surface Oxygen Groups by Gas-Phase Oxidation and Its Implications for Lithium Ion Batteries

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Multi-walled Carbon Nanotubes (CNT) have proved to be a versatile material for lithium ion batteries (LIB). They can be used as active material[1], self-supporting electrodes[2] or conductive additive[3]. Like with graphite, one of the most important aspects of CNT used as negative electrode is the formation of the solid electrolyte interphase (SEI) and the initial charge loss (ICL) during first discharge[4].

It was recently shown that SEI formation is not only dependent on the electrolyte, but, as it is forms on the surface of the electrode material, also depends on the active surface area and the amount of surface oxygen groups[5]. However, a conclusive knowledge about the role of the surface oxygen chemistry during SEI formation is still missing.

Using CNT as active material, we were able to find a correlation not only between the concentration but also the type of surface oxygen groups and the amount of ICL. In consequence, we changed the type of oxygen groups on the surface by means of gas-phase oxidation[6] and obtained CNT with a significantly decreased ICL caused by ex-foliation compared to CNT in liquid HNO₃[7]. Not only does this result shed new light on CNT modifications for a more target-oriented research, it might also help to under-stand the SEI formation on other carbon materials.

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Generation and Stabilisation of Stilbene Dianion with Ionic Liquids or TCNQ

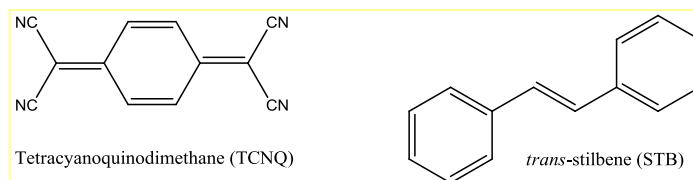
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Stilbene (STB) and tetracyanoquinodimethane (TCNQ) are examples of π -systems that have interesting electronic properties.

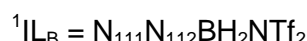


Although electrochemical reduction of TCNQ is chemically reversible in most organic solvents, access to long lived STB dianion was previously unsuccessful, owing to its high reactivity and possible reaction with adventitious proton in the solvent/ electrolyte system.

However, in this study, we were able to generate and stabilise stilbene dianion at room temperature for the first time via use of boronium based ionic liquid¹ (IL_B) as a solvent-electrolyte system. This is because IL_B has the desired characteristics of high electrochemical stability extending to very negative potentials, and the absence of proton donation properties. Important findings of this work clearly establish that ionic liquids may provide better alternative of the traditional protic or organic solvents for the electro-reduction of organic molecules.

Another interesting finding is noticed when the electro-reduction of stilbene is performed in the presence of strong electron acceptor such as TCNQ. Thus, Cyclic voltammetry of STB and TCQ or the chemically-synthesized STB-TCNQ charge transfer complex gave rise to four one-electron chemically and electrochemically reversible processes. Based on the formal reversible potential of each redox couple, the first two processes are assigned to reduction of TCNQ into $TCNQ^{\cdot-}$ and $TCNQ^{2-}$, whereas the second two are associated with $STB^{0/-1}$ and $STB^{-1/-2}$ couples.

This behavior implies that the association and interaction between the complex components (STB and TCNQ) and the intra- molecular interactions help to stabilise the generated stilbene dianion, by preventing it from reacting with adventitious proton.



Electrochemical Switching of Polymer Brushes Grafted Onto Conducting Polymer Films

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We demonstrate the electrochemical switching of conformation of surface-bound polymer brushes, by grafting environmentally sensitive polymer brushes from an electrochemically-active conducting polymer (ECP). Using atom transfer radical polymerization (ATRP), we grafted zwitterionic betaine homopolymer and block copolymer brushes of poly(3-(methacryloylamido)propyl)-N,N'dimethyl(3-sulfopropyl)ammonium hydroxide) (PMPDSAH) and poly(methyl methacrylate)-b-PMPDSAH, from an initiator surface-coupled to a poly(pyrrole-co-pyrrolyl butyric acid) film. The changes in ionic solution composition in the electrical double layer at the surface resulting from oxidation and reduction of the ECP trigger a switch in conformation of surface-bound polymer brushes, demonstrated here by electrochemical impedance spectroscopy (EIS). The switch is also dependent upon temperature and salt concentration in solution in a way that is analogous to the salt- and temperature-dependent solubility and aggregation of similar betaine polymers in aqueous solution. We interpret the behavior in terms of the balance of intra- and inter-molecular interactions controlling the transition to a “super-collapsed” state on the surface. We speculate that the synergistic combination of properties embodied in these “smart” materials may find applications in electrochemical control of surface wetting and of interaction with biomolecules and living cells.

Regain of Electrochemistry on Passivated Electrodes Decorated by Gold Nanoparticles: Thickness Dependence of the Passivating Layer

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Recently it has been shown that attaching gold nanoparticles (AuNPs) onto the ends of otherwise passivating organic layers opens up conducting pathways through which electron transfer can proceed as though the organic layer is not even present [1]. According to Chazalviel theory [2], the key point of this surprising behaviour is that electron transfer from metal to metal is intrinsically easier than transfer between metal and redox system by many orders of magnitude; however, thickness of the passivating layer plays a major role as the limiting factor. Since well organised self-assembled monolayers are not achievable for long alkyl chains upon 16 carbon units, because of limitation in source of longer molecules, here we take advantage of the cathodic electrografting of in situ generated aminophenyl monodiazonium cations to build multilayered films on glassy carbon electrodes (GCE). Ellipsometry showed different deposition times result in different polymer thicknesses from 1.43 nm to 3.46 nm (Fig. 1) and these deposited multilayers had progressively greater blocking abilities towards ruthenium hexamine as they got thicker. Fast electron charge transfers however are regained once AuNPs are immobilized to these passivated electrodes. More interestingly, thickness dependence of charge transfer through GCE-polymer-AuNP construct was observed with electrochemical impedance spectroscopy, with no NP-mediated electron transfer up to the polymer thickness of 3.5 nm (Fig. 2).

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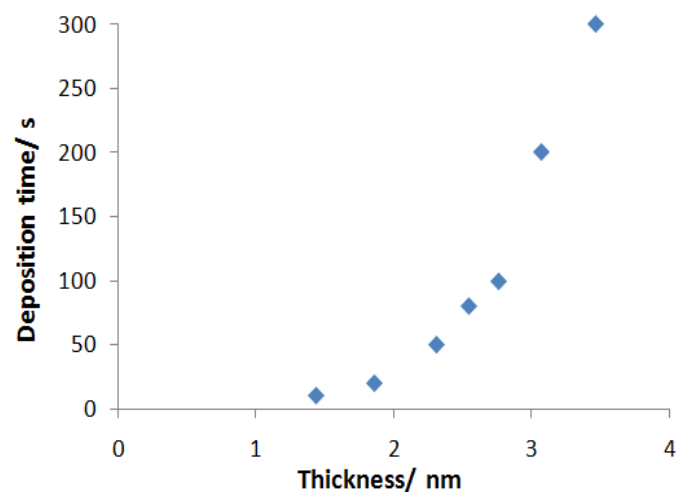


Figure 1. Thickness of the deposited layers obtained by Ellipsometry as a function of deposition time.

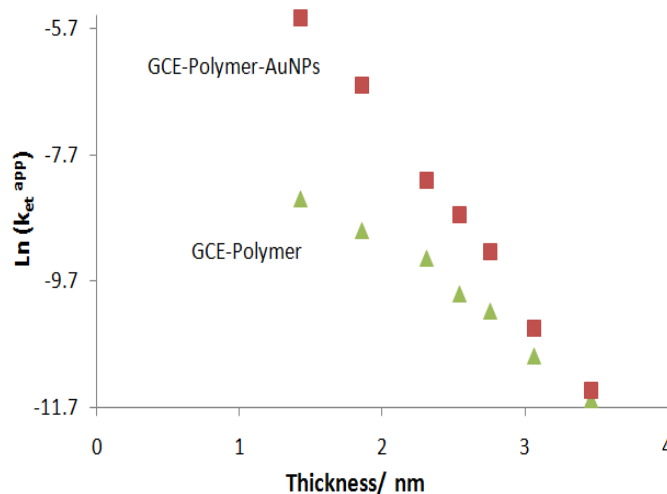


Figure 2. Rate constants for electron transfer for modified GC electrodes before/after the immobilization of 27 nm AuNPs as a function of the polymer thickness.

Extraction of metal ions from aqueous solutions with methimazole-based ionic liquids

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The new 2-butylthiolonium bis(trifluoromethanesulfonyl)amide ([mimSBu][NTf₂]) ionic liquid (IL) has been characterized and used for the extraction of copper (II) ions from aqueous solution. The copper complex formed in the IL has been characterized by cyclic voltammetry and UV-vis, Raman and NMR spectroscopies. The microextraction of Cu²⁺ with [mimSBu][NTf₂] was followed by in situ cyclic voltammetry. Cu²⁺ preferentially binds with the cation and Cu⁺ with the anion of the ionic liquid. Thus, the Cu^{2+/+} couple exhibits a novel switching mechanism. The pH of the aqueous phase decreases as Cu²⁺ is extracted into the IL. The increase of the acidity in the aqueous phase is due to the water assisted partial release of the hydrogen attached to the N(3) of the imidazolium ring. Water also promotes the incorporation of Cu²⁺ into the ionic liquid. The extraction process does not require deliberate addition of a complexing agent or pH control of either the aqueous or IL phases. Importantly, [mimSBu][NTf₂] can be recovered by washing with a strong acid. Analogous studies have been undertaken on the extraction of silver(I) and gold(III) using related ionic liquids.

Electro-controlled swelling of a full polymeric 3-D conducting monolithic device

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Controlled release systems have shown great importance in biomedical and environmental applications. Consequently, the development and characterization of new materials potentially able to be applied in these systems is a matter of relevant importance.

The present work details the synthesis and electrochemical characterization of four types of compacted polymeric 3D hydro-sponges made of polypyrrole microtubules. During the synthesis, particles with cylindrical geometry were employed as sacrificial templates, promoting polypyrrole's growth on their surfaces in order to form tubular structures. Hydro-sponges were then obtained by assembling synthesized PPy microtubules into networks under static conditions. Once hydro-sponges are made of a conducting polymer, the novelty of the work relies on controlling not only the swelling but also the artificial-muscle properties due to the electrical-induced volume change of Ppy in function of the variation of its oxidation state. As disclosed here, both behaviors are extremely related to the morphology of the four obtained Ppy made hydro-sponges. The morphology and, consequently, the hydro-sponges properties can be modulated in function of the conditions employed during the synthesis, which opens perspectives to achieve different materials with potential application in different types of controlled release devices.

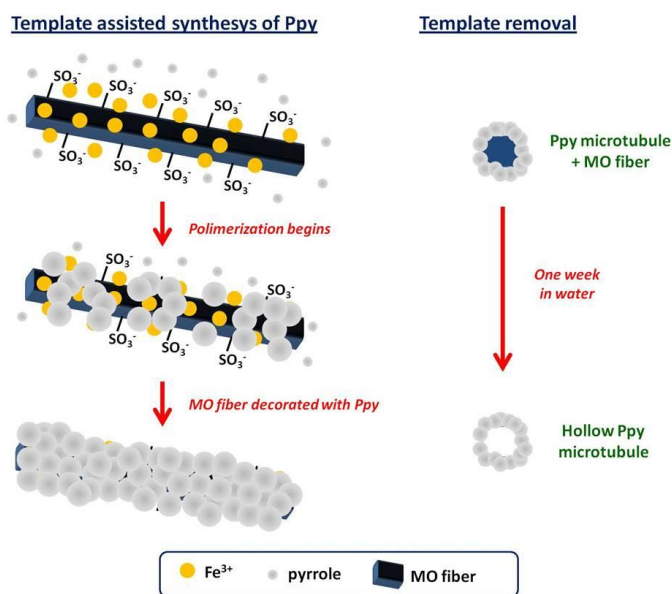


Figure 1: Scheme showing the template assisted Ppy synthesis and posterior template removal. Note that in this cartoon, Fe^{3+} oxidants are complexed in MO surface, leading almost exclusively to a polymerization around the template.

A New Ion-to-Electron Transducer for Solid-State Polymeric Ion Sensors Based on Ferrocene Tagged Polyvinyl Chloride

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Plasticized ion sensing membranes incorporating ferrocene tagged polyvinyl chloride (Fc-PVC) have been investigated as potential new ion-to-electron transducers in all-solid-state polymeric ion sensors. In this work, we oxidized the plasticized Fc-PVC membranes using chronoamperometry, and studied the oxidation of ferrocene moieties and ensuing ingress of counter-anion using synchrotron radiation X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) in conjunction with argon ion depth profiling. Surprisingly, this research demonstrated that the Fc-PVC material is oxidized and accumulated at the underlying substrate of the solid-state electrode, thereby creating a layered structure of electroactive and non-electroactive materials in the plasticized electrode. This outcome has important ramifications for the application of plasticized PVC membranes in electrochemistry, e.g., new solid contacts can be created by dissolving a redox mediator in the plasticized PVC membrane and activating the electrochemistry to create an underlayer of redox buffering material.

Use of Mobile Cell Phone for the Generation and Detection of Electrogenerated Chemiluminescence in Low Cost Sensors

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The emergence of paper as a microfluidic material has recently begun to stimulate considerable interest from researchers interested in producing low-cost sensors. Moreover, the use of cell phones and similar devices for signal transduction is receiving a growing amount of attention. While the majority of the work reported to date has focused on colorimetric detection, we recently reported electrogenerated chemiluminescence (ECL) detection with paper-based microfluidics using a common mobile camera phone. [1]

Colorimetric detection with a mobile phone is attractive because of how cheaply it can be accomplished, however it suffers from the dependence on ambient light, which is difficult for field use especially in third world countries. ECL has an advantage over colorimetric detection because it is independent of ambient light. ECL is also advantageous over electrochemical detection because electrochemical detection requires extra instrumentation, whereas we will show that ECL can be initiated, captured and analysed with a mobile phone alone.

In this presentation we will describe an arrangement for sensing in developing countries based on ECL, composed of paper microfluidics, screen printed electrodes (SPEs) and a mobile phone. We will demonstrate the initiation of the ECL reaction using a voltage applied by the mobile phone itself via the earphone jack. With this technique it makes an ECL paper-based sensor a plausible solution for diagnostics and other sensing in resource-poor environments.

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Adsorptive stripping voltammetry of lysozyme via adsorption-desorption at liquid|liquid microinterfaces

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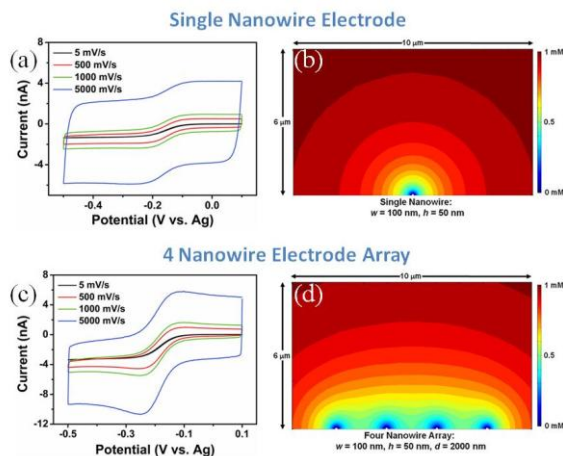
Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) is based on charge transfer across the polarized interface, formed when bringing two electrolyte solutions (aqueous and organic) into contact. This provides the possibility for label-free detection of biomolecules. In this work, lysozyme, a globular protein, has been studied at an array of liquid|liquid micro-interfaces. These smaller interfaces experience a higher mass transport flux, resulting in a higher current density which is beneficial from a sensing point of view. The mechanism of lysozyme detection at the μ -ITIES is believed to follow an initial protein adsorption process at the polarized interface followed by facilitated transfer of organic phase anions. Thus, lysozyme adsorption properties at the ITIES were employed to try to achieve lower limits of detection. Adsorptive Stripping Voltammetry (AdSV) is a widely used strategy based on pre-concentration of the target analyte onto mercury or solid electrodes. In this work, adsorption of lysozyme at the polarized liquid|liquid micro-interfaces is suggested to involve kinetic control. Lysozyme multilayer formation is proposed at long pre-concentration times, which is in agreement with previous work performed by Herzog et al. This involves a saturation surface coverage of 550 pmol cm^{-2} and a linear range of $0.05\text{-}1 \text{ }\mu\text{M}$ of lysozyme for prolonged pre-concentration steps. With a pre-concentration period of 5 minutes, AdSV demonstrated a limit of detection of $0.03 \text{ }\mu\text{M}$ ($0.44 \text{ }\mu\text{g/ml}$), which is two orders of magnitude lower than previous literature methods at ITIES for protein detection. These results provide the basis for a new analytical approach for label-free protein detection.

Discrete Gold Nanowire Arrays: An Electrochemical Study

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A key advantage of employing nanoscale electrodes is that it enables high densities of sensors to be fabricated in a much smaller footprint at key substrates, such as on a silicon chip, thus yielding much higher information-generating capability per device. In electrochemistry, attempts to work at very small (sub-micrometer) electrode sizes at silicon substrates, particularly discrete individual nanowires have not been reported extensively in the literature¹. This reflects the difficulty in both fabrication and integration of nanowire electrodes as functional sensing elements in functional devices. However, the drive to developing new sensor devices that exhibit increased sensitivity with the ultimate goal of achieving single molecule detection remains a key technological motivation in this area²⁻³. In this regard, increasing the number of sensing elements, by fabricating arrays of discrete nanowires, offers the potential to achieve enhanced sensitivity at a much lower foot print when compared to ultra-microelectrodes

In this talk, I will present discrete gold nanowire arrays fabricated using electron beam lithography which were designed to possess sufficient inter-nanowire spacing so as to prevent overlap of diffusion layers of adjacent nanowire electrodes. A chip design was implemented that comprised twelve separate electron beam fields containing either a single nanowire or nanowire arrays. The chips also contained on-chip counter electrodes, SiNx passivation and on-chip contact pads located at the chip periphery that facilitated direct electrical probing and thereby eliminated the requirement for time consuming microelectronic packaging approaches. Critical dimensions of nanowire and nanowire arrays were characterised using a combination of optical, probe and electron microscopy. Electrical and electrochemical characterisation of the nanowire arrays was undertaken to explore the diffusional process occurring at arrays with increasing number of nanowires. A simulated analytical study was undertaken to provide further insight into mass transport to the electrodes. Electric field simulations were also undertaken to elucidate the effects of on-chip interconnection metallisation on interfacial capacitance. Finally, application of pulse voltammetric techniques was used to explore future analytical possibilities employing nanowire arrays as sensor elements.



(a) CV measurements recorded at single nanowire electrode and an array 4 nanowires (c.) were based on 1 mM $\text{Ru}(\text{NH}_3)_6^{3+}$ in 10 mM PBS at a range of scan rates vs. Ag. Simulations are of a plane perpendicular to rows of nanowire electrodes. (B & D) In all cases bulk concentration is 1 mM and $D_0 = 5.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at a scan rate of 5000 mV s^{-1} .

Acknowledgements SFI – RFP (09/RFP/CAP2455) & EU FP7 CommonSense (261809)

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Towards the Electrochemical Quantification of the Strength of Garlic

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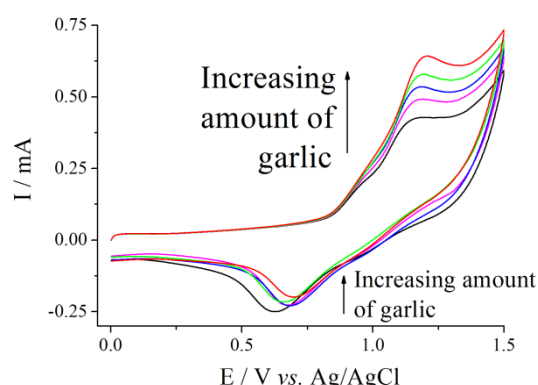
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Millions of tonnes of garlic are produced annually worldwide, to be used widely in medicinal supplements and cookery.^[1] As the strength of flavor varies from species-to-species and crop-to-crop, new garlic sources for large scale applications are investigated by organoleptic testing using a trained panel of human experts, often after dilution in sour cream. The potential spoiling of garlic during long-term storage is also monitored by periodic organoleptic testing.

Electroanalysis is a versatile technique that can be used to prepare minaturised, inexpensive sensors that can be operated by non-experts, *c.f.* amperometric glucose sensor strips. Screen-Printed Carbon Electrodes (SPCEs) represent widely available, versatile, portable, disposable amperometric systems that can operate on μL -scale samples.^[2] Adsorptive stripping voltammetry has been previously used at SPCEs to accurately quantify the 'heat' of chilli sauces in line with organoleptic measures.^[3]

In this work^[4,5] we have successfully identified a simple but sensitive technique towards the electroanalytical quantification of the strength of garlic at SPCEs, which holds the potential to replace organoleptic testing in relation to garlic potency. A rich variety of disulfide compounds contribute to the flavour and fragrance of garlic, although diallyldisulfide has been consistently found to be the most overwhelmingly abundant extractant from processed, raw garlic.^[6] When electrochemically generated from bromide ions (Br^-), Br_2 was found to react chemically with disulfide compounds and regenerate Br^- , enhancing the current of the Br^- oxidation peak in line with diallyldisulfide concentration.

Shaking garlic puree by hand in acetonitrile was found to efficiently extract disulfides present in the garlic. The voltammetry of the Br^-/Br_2 mediator couple was proportional to both the concentration of garlic present in the sample, and the historical strength of garlic from the source (China or Spain). Both Edge-Plane Pyrolytic Graphite (EPPG) electrodes and disposable Screen-Printed Carbon Electrodes (SPCEs) could be used, with a limit of detection of $67\ \mu\text{M}$ determined for the diallyldisulfide analogue, dipropyldisulfide.



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3. POSTER ABSTRACTS.

Electroactive Monolayers on n-Type Silicons

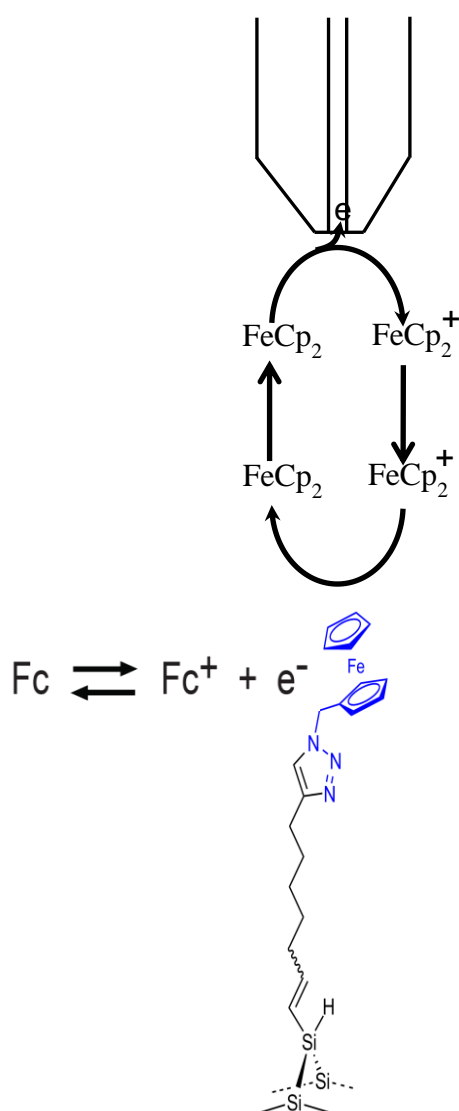
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In this study, covalent immobilization of well-defined acetylene-terminated organic monolayers were prepared on hydrogen terminated n-type Si from single step hydrosilylation procedure from 1,8-nonadiyne, then azidoferrocene was attached on the distal end of alkyne by click reaction. The surface was characterized by XPS and found no evidence of SiO_x contaminants for SAMs. In addition, after clicking azido ferrocene on the distal end of alkyne, Scanning electrochemical microscopy (SECM) in feedback mode was applied to study electronic communication between the ferrocene (Fc) centre and the underlying semiconductor surface.



Chronoamperometric study of ion transfer at nano- and micro-ITIES arrays

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Ion-transfer processes at interfaces between immiscible electrolyte solutions (ITIES) provide a platform for the detection and determination of species that do not exhibit redox-activity. The miniaturization of these interfaces brings about enhanced diffusional flux which in turn leads to improved analytical sensitivity. In this work, the behaviour of arrays of micro- and nano-scale ITIES under potential step chronoamperometric (PSCA) conditions is compared both theoretically and experimentally, using the ion-transfer of tetrapropylammonium cation (TPrA⁺) as a model process. The micro- and nano-ITIES arrays were formed at microporous silicon and nanoporous silicon nitride membranes, respectively. Experimental currents for diffusion-controlled currents were compared to published models (e.g. Cottrell, Shoup and Szabo) and to published chronoamperograms at solid electrodes. Information on the response time and the influence of pore resistance was also determined. Finally, the chronoamperometric responses of the micro- and nano-ITIES arrays as a function of the analyte concentration and the applied step potential were studied. The new information generated will help to improve the analytical detection sensitivity of chemical or biochemical substances based on ion-transfer amperometry or voltammetry.

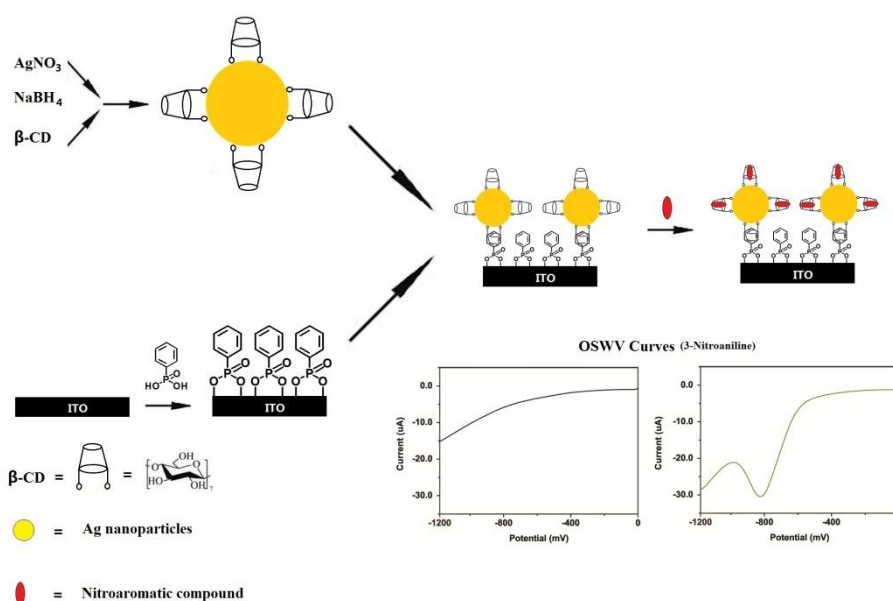
Detection of Trace Nitroaromatic Isomers Using AgNPs/ β -Cyclodextrin Modified ITO Electrodes

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Abstract: Determination of nitroaromatic compounds was investigated at a AgNPs/ β -cyclodextrin composite modified ITO electrodes in 0.2 M KCl aqueous solution (pH 7) using square wave voltammetry (SWV). This assay relies on the different reduction peak position of various nitroaromatic isomers, the different inclusion binding strength of the nitroaromatic isomer guests to β -CD host and excellent electron transfer ability of AgNPs. After 10 min incubation in a solution with different single nitroaromatic compound, special reduction peak at different position from -550 mV to -913 mV appeared in SWV measurements, which indicated that all nitroaromatic compounds could not only be detected but distinguished from each other by the composite modified ITO electrode, the detection limits can be as low as 1×10^{-7} mol/L.



Electrochemical behavior of proteins at arrays of liquid-liquid microinterfaces

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The electroactivity of proteins at liquid-liquid interfaces provides the basis for a simple means of label-free detection of biomolecules. Unlike conventional electrochemistry, this is based on ion transfer at the interface between two immiscible electrolyte solutions (ITIES), namely an aqueous electrolyte solution and an organic electrolyte solution. This can overcome problems associated with redox-inactive molecules or molecules which have difficulty associated with their redox chemistry, such as the detection of dopamine in the presence of ascorbic acid. Here, miniaturised liquid-liquid interfaces were utilised by supporting the organic phase in a membrane which contains an array of micropores. This miniaturisation of the interface allows for improved mass transport, increased current density and reduced ohmic potential drop. The behaviour of the heme-containing protein, myoglobin, was investigated at the μ ITIES. The protein was shown to adsorb at the interface and facilitate the transfer of the organic anion to the aqueous phase. The electrochemical response was shown to be linear in the range of 1-6 μ M, with a corresponding surface coverage of 5-35 pmol/cm². The reverse peak currents was found to be proportional to scan rate indicating a desorption process. The detection of the protein was only possible when the pH of the solution was below the pI of the protein. The steady-state behaviour of tetraethylammonium cation transfer was disrupted on the forward sweep, indicating the presence of adsorbed protein at the interface. Increasing the ionic strength of the solution resulted in enhanced peak currents, possibly due to aggregation of protein precipitates in the aqueous solution. Uv/vis absorbance spectroscopy was used to investigate the effects of various aqueous solutions on the structure of the protein, and it was shown that at low pH the protein is at least partially denatured. The effects of addition of surfactant to the system were also explored, the surfactant AOT when added to the organic phase showed an increase in the desorption peak current of haemoglobin, myoglobin and cytochrome c by more than 5-times that obtained without AOT. Repetitive cyclic voltammetry of cytochrome c showed that in the presence of surfactant there was an enhancement of the signal caused by a build-up of protein at the interface. This provides the basis for future work with surfactant modified systems with the aim to increase the sensitivity and limits of detection for protein detection.

Electrochemistry at the Liquid-Liquid Interface of a Droplet of Water and 1,2-Dichloroethane

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) is important in electrochemical studies of ions that do not possess redox reactivity at a solid electrode/solution interface over a prescribed potential window. Here, we present a simple approach based on a “hanging water drop” (see Figure 1) for the exhaustive transfer of ions from the aqueous phase to an organic phase with the aim of producing a calibration free coulometric ion sensor.

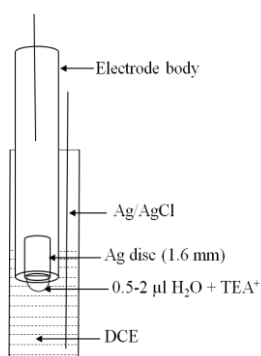


Fig. 1: Schematic presentation of the electrochemical set up.

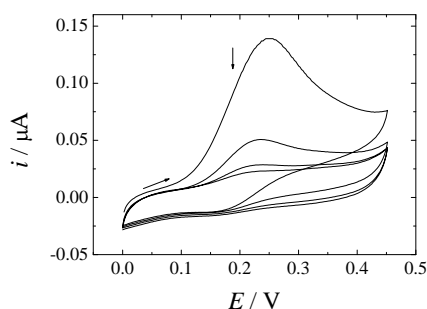


Fig. 2: Cyclic voltammogram (four cycles) measured at the interface between 2 μl water drop (containing 0.05 mM TEA^+) and 1,2-dichloroethane (DCE) at a scan rate of 5 mV/s.

An irreversible asymmetric voltammogram is obtained at the “hanging water drop” (see Figure 2), which is due to different modes of diffusion during ion extraction and accumulation. Due to the hemispherical shape of the water droplet, both semi-infinite linear and radial diffusion are contributing to influx and efflux of ions during extraction and accumulation of ions, as has been confirmed via the scan rate dependence of the ion extraction process. It has been observed that just one cycle at a scan rate of 1 mV s^{-1} is sufficient for complete removal of tetraethylammonium (TEA^+) from a water droplet of $0.5 \mu\text{l}$. The enhanced rate of diffusion during the efflux of ions makes the “hanging water drop” a promising system for calibration free coulometric ion sensors. To the best of our knowledge, there are no previous studies of this kind, noting that work by other authors [1, 2] has utilized a film or a droplet of organic solvent comprising a redox species in electron transfer studies with ITIES.

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Arsenic Detection using Functionalised Metal Nanoparticle Modified Screen Printed Electrodes

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Water is becoming the most valuable resource for survival of mankind. The situation is more severe in developing countries where most of the available potable water sources are polluted with various natural and anthropogenic contaminants. Arsenic is one of such contaminant mostly coming from natural sources and is affecting billions of people worldwide. Groundwater arsenic contamination in the Bengal delta has been termed as the largest chemical poisoning in history [1]. Among various solutions available for mitigating the arsenic problem, nanotechnology holds good promise since nanomaterials can provide unique solutions in terms of reduced costs, improved ability to selectively remove contaminants, durability, and size of the device [2,3]. Detection of arsenic is crucial to identify the safe sources and to monitor the efficacy of treatment units. Arsenic sensors based on nanotubes, nanoparticles and nanowires have been extensively studied [4,5]. The present study deals with development of screen printed electrode modified with functionalized metal nanoparticles for stripping voltammetric detection of arsenic. Optimization of various parameters namely deposition potential, deposition time, type and concentration of electrolyte, etc. have been conducted. These electrodes have also been tested using arsenic contaminated natural water collected from arsenic affected areas in India and the modified electrodes showed excellent recovery. The functionalised metal nanoparticle modified screen printed electrodes show good selectivity, sensitivity, reproducibility and linear response for electrochemical detection of arsenic.

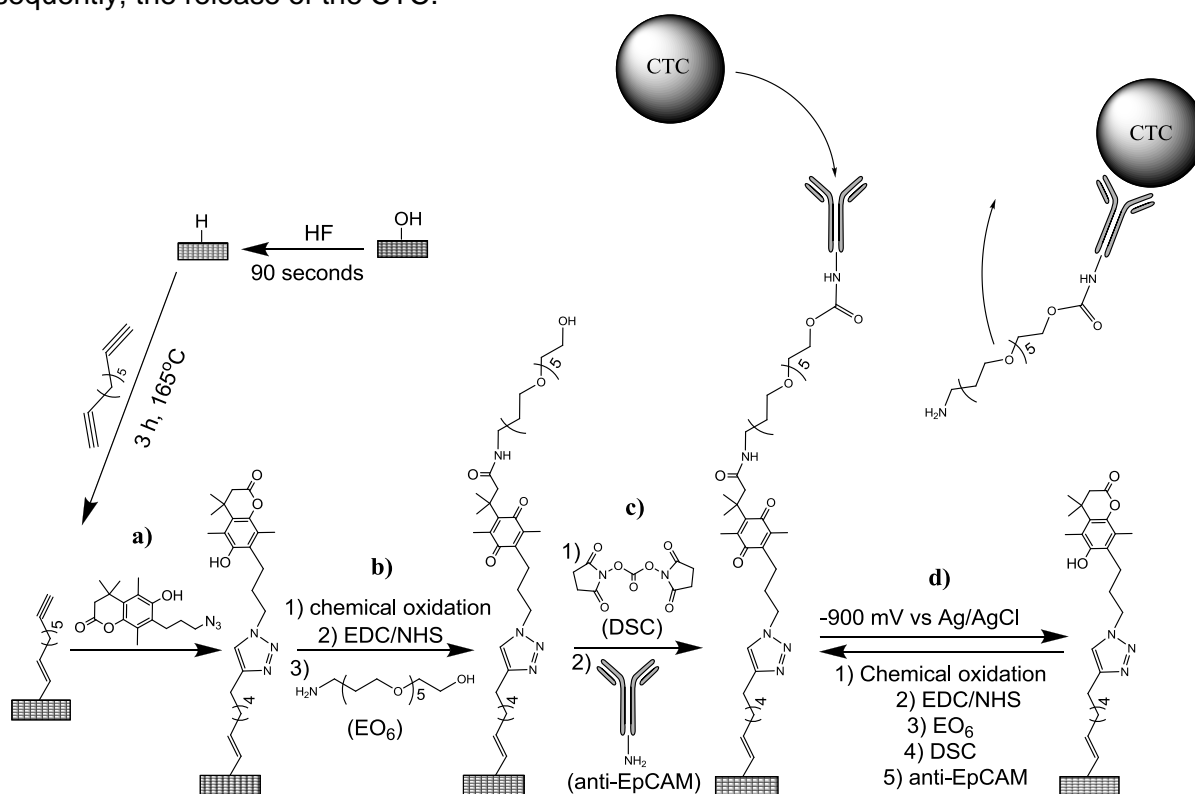
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Capture and Releasing Rare Circulating Tumour Cells Using Electrochemically-Switchable Surfaces

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Circulating tumour cells (CTCs) provide a potentially accessible source for detection, characterisation and monitoring the progression of non-hematological cancers. However, CTCs shed from primary and metastatic cancers are mixed with blood components and are thus rare but dangerous. The work herein describes a way to capture and release live CTCs by using electrochemically-switchable molecules bound to a silicon surface to capture cells and once poised at an appropriate potential, cleave and release the cell. In order for electrochemistry to take place, oxide-free silicon surfaces were created by modifying them with a well-defined, passivating, acetylene-terminated monolayer. The electrochemically-switchable molecule was then subsequently attached to the surface via a “click” reaction. This switchable molecule was chemically oxidised to immobilise an antibody on the surface that selectively binds to antigens (EpCAM) overexpressed in the MCF-7 breast cancer cell line. Applying a -1800 mV potential to the surface led to the reduction of the switchable molecule and subsequently, the release of the CTC.



A Langmuir Trough study of the interactions between syndiotactic-PMMA and ISE-dopants probed by neutron/x-ray reflectometry.

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In this research, materials used traditionally in ion-selective electrode (ISE) membranes will be studied in relation to their electrochemical and physicochemical responses to gases. Accordingly, the research is expected to extend materials available for gas sensing, while also providing a deeper understanding of interference effects by ambient gases on the ion sensing response(s) of these materials – critical for the stability of all-solid-state polymeric ion sensors. An in depth understanding of how the physicochemical and microscopic properties of poly(methyl methacrylate) (PMMA) are affected by certain additives is expected to enhance the use of PMMA in the chemical sensing of gases and ions. In this work, the interactions between deuterated PMMA molecules and various lipophilic ion exchanger salts deposited at the air water interface will be studied to elucidate their impact on the cohesivity and packing of polymer molecules in the sensing film. Accordingly, neutron reflectometry (NR) studies of thin films of polymers spread across the aqueous/air interface of a Langmuir trough will be performed at different dopant concentrations. The monolayer properties were monitored simultaneously by NR, while X-ray reflectometry (XRR) measurements were undertaken to provide complementary scattering information on the polymer sensing films. To elucidate the impact of the glass transition temperature, T_g , on the polymer matrix and concomitant behavior of the system, the experiments were repeated with deuterated poly hexyl-methacrylate dPHMA, which has a T_g below room temperature, noting that polymers with T_g values below room temperature are highly desirable since this circumvents the need for a plasticizer in ISE membranes. These experiments will lead to a substantially improved understanding of the response mechanisms of the underlying electrochemical processes, and how they are affected by doping with molecules of various structures and properties, thus guiding the optimization of these sensing elements for improved sensitivity and selectivity.

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Towards a Multiple-Analyte Sensor by use of Dispersible Modified Au@Fe₃O₄ Nanoelectrodes

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The concept, which we refer to as 'dispersible electrodes', involves using modified gold-coated magnetic nanoparticles as the active elements in scavenging and then detecting ultra-trace amounts of analytes in solution. The fact that the dispersible electrodes are magnetic provides a means by which the analyte can be captured and brought back to the sensing surface for detection.^[1] In conventional electrochemical analysis with a single monolithic electrode the analyte takes a long time to reach the sensing surface resulting, in long response times for low concentrations of analyte. Nano-sized dispersible electrodes solve this problem as they are released in high number concentration in the test solution to capture the analytes of interest in a reasonable time frame and then brought to an electrode surface using a magnet. Previous research in our group has demonstrated that 50-180 nm peptide-modified gold coated magnetite nanoparticles with 3-mercaptopropionic acid as the thiol have been used as dispersible electrodes for the capture and detection of Cu²⁺.^[2]

This current research focuses on analysis of other metals such as Pb²⁺ and Cd²⁺ as single analytes leading to the development of a multiple analyte sensor. Multiple-array sensors involve functionalizing the nano-sized dispersible electrodes with different analyte seeking molecules. We report the method of peptide modification of the dispersible electrodes using thioctic acid in order to attach the peptide angiotensin and detect Pb²⁺. XPS results obtained showed that we were able to successfully attach the thiol by the emergence of peaks in the C 1s spectra, centered at 286.2 eV and 281.9 eV. Peptide modification was also confirmed by four component peaks at binding energies of 396, 397.5, 398.5 and 399.6 eV, see figure 1. SWV results showed a reduction potential of Pb²⁺ at -0.366 eV, see figure 2. Future studies will include use of the magnetite nanoparticles in multiple element analysis and bacteria assay.

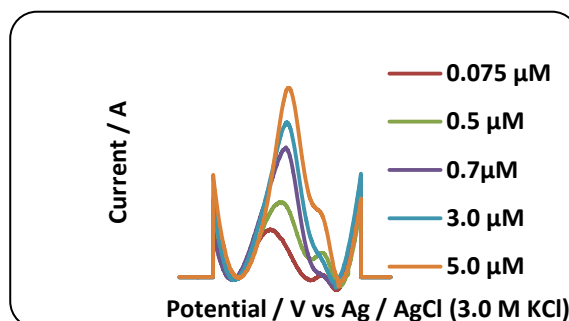
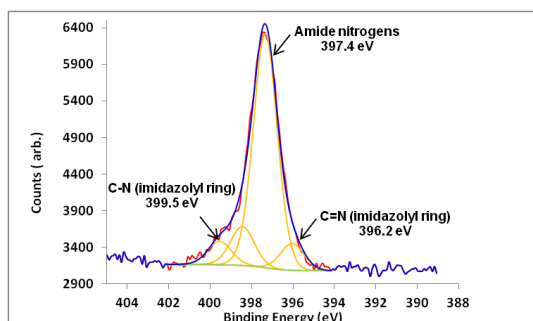


Figure 1: XPS spectrum of nano-particle electrodes modified with thioctic acid and angiotensin I

Figure 2: Square-wave voltammograms at thioctic acid - angiotensin I modified nano-particle electrodes measured in 50 mM ammonium acetate (pH 7.0) and 50 mM sodium chloride

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Enhanced electron transfer at a glassy carbon electrode modified by covalently attached graphene oxide

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In this paper, a modified Schmidt reaction was used to covalently attach graphene to a glassy carbon electrode in order to improve electron transfer at the electrode, and thereby enhance the analytical detection at the electrode. Initially, graphene oxide was prepared by oxidising 1-2 μm graphite powder using a modified Hummers-Offeman method. Meanwhile, glassy carbon electrodes were oxidised, and then modified by an alternative Schmidt reaction to introduce amine functionality to the electrode surface. In this way, the carboxylic acid functional groups on graphene oxide would react with amines on the glassy carbon, resulting in graphene covalently bonded to the electrode surface. The graphene-modified glassy carbon electrodes were characterised by cyclic voltammetry of $\text{Ru}(\text{NH}_3)_6^{2+/3+}$, $\text{Fe}(\text{CN})_6^{4-/3-}$, and ferrocenecarboxylic acid. Compared to bare glassy carbon electrodes, the graphene-modified electrodes showed a 24%-57% increase in redox peak current to both the negative and neutral species, and a 12% increase for the positive species, as the redox reaction was enhanced by the electron transfer properties of graphene. Electrochemical impedance spectroscopy was also employed to study the characteristics of the electrode-solution interface in $\text{Fe}(\text{CN})_6^{4-/3-}$. After modification, there was no significant change to the resistance of solution. However, the electron transfer resistance was reduced by 85% after modification, which was complementary to the cyclic voltammetry study. The electrode was further applied to the electrochemical detection of the antioxidant, ascorbic acid, in tea samples.

Electrochemically Induced Electro/Electrolyte Interfaces of Solid Oxide Fuel Cells

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In solid oxide fuel cells (SOFCs), electrode/electrolyte interfaces are extremely important for the fundamental understanding of the electrochemical processes such as activation process. Activation process can be defined as the enhancement of the electrochemical performance or activity of a SOFC cathode (e.g., Sr-doped LaMnO₃, LSM) under the polarization/current passage treatment [1]. The enhancement is characterized by the rapid decrease in the electrode polarization (interface) resistance with the polarization treatment. For practical cells, this enhancement process can last tens or hundreds of hours. It is, therefore, fundamentally important to understand the activation phenomena for the efficient and reliable operation and design of SOFCs.

Figure 1 shows AFM images of the LSM/YSZ interface formation under different cathodic current polarization conditions. After polarization treatment, there is formation of nano-sized contact marks or islands on the surface of YSZ electrolyte, as shown by circles in the figure. With the increase of the current densities, the number of contact islands grows. Preliminary results indicate there is close correlation between the activation process and the electrochemically induced interface formation for the O₂ reduction reaction of SOFCs.

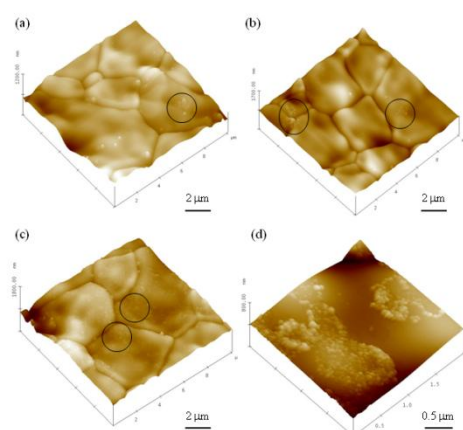


Figure 1. AFM images of *in situ* sintered LSM/YSZ electrolyte interface after polarized at (a) 100 mAcm⁻²; (b) 500 mAcm⁻²; (c) 1000 mAcm⁻²; and (d) high magnification of (c). LSM electrode was removed by HCl treatment.

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Exploitation of Protic Ionic Liquids as Electrolytes for Electrodeposition of Metals

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Using room-temperature ionic liquids (RTILs) for electrodeposition is very appealing. RTILs exhibit notable thermal stability, low vapor pressure, great ionic conductivity and wide potential window which make it suitable for the processes [1]. RTILs are generally divided into 2 classes, namely aprotic ionic liquids (AILs) and protic ionic liquids (PILs). Most current research on electrodeposition concentrates on using AILs. To the best of our knowledge PILs have never been used for electrodeposition of metals. PILs are formed by a variety of proton transfer and association equilibria of Bronsted acids and bases [2]. The simple synthetic procedure is the major advantage for large scale industrial application in term of cost over AILs.

In this presentation, we study the electrodeposition of a number of metals from PILs. The metals of interest include Ag, Co, Cu, Zn and Ni and etc. The electrodeposition has been carried out on a number of substrates such as GC, Au, Pt and ITO. The electrodeposition processes have been studied using cyclic voltammetry and chronoamperometry. The electrodeposited metals have been examined by using optical microscopy, scanning electron microscopy and X-Ray techniques.

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Low cost LEECs based on room temperature ionic liquids

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Light emitting electrochemical cells (LEECs) use considerably less reactive components than organic light emitting devices (OLEDs). Combined with easier manufacturing methods needed to produce, LEECs based on transition metal luminophores may offer a greater diversity of applications with enhanced quantum efficiency, longer lifetimes and shorter turn-on times.

Recently, room temperature ionic liquids (RTILs) have been employed in the fabrication in LEECs as they offer a wide variety of properties favorable to enhance LEEC function to make them suitable for commercial applications.

This poster presents preliminary results using a screen printed electrode based device towards making novel LEECs suitable for a variety of commercial applications.

A modified concentration variable for facile standard addition calculations using Excel spreadsheets, together with a simplified estimation of relative uncertainty for analyte determinations

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The analytical calibration technique of standard additions is used to mitigate matrix effects and attempts to deliver unbiased results when the test solution varies in an unpredictable manner. In one manifestation, initial measurements are performed on a solution containing an unknown quantity of analyte and then successive additions of known amounts of analyte are made, with the analytical measurements being repeated. Such a calibration method is well suited to ultra-trace analysis by stripping voltammetry, atomic absorption or UV-visible absorption.

The usual independent variable for this standard addition method is 'added concentration', the difference between the actual and initial analyte concentrations, $c - c_0$. This leads to mathematical complications since c_0 is the (unknown) sought value. With a modified concentration variable not dependent on c_0 , least-squares calculations for linear calibration are much more straightforward and may be accomplished directly with inbuilt functions in MS Excel. The availability of statistical output in Excel offers additional utility for assessing the standard errors of fitted parameter values and the calculated analyte concentration.

A simplified estimate of the relative uncertainty of c_0 may be performed geometrically, as a guide to the inherent reliability of a particular standard addition procedure. If the initial signal is measured as I_0 , it can be shown that the cumulative amount of added analyte should be sufficiently large to generate a final signal of $I_n > 2I_0$.

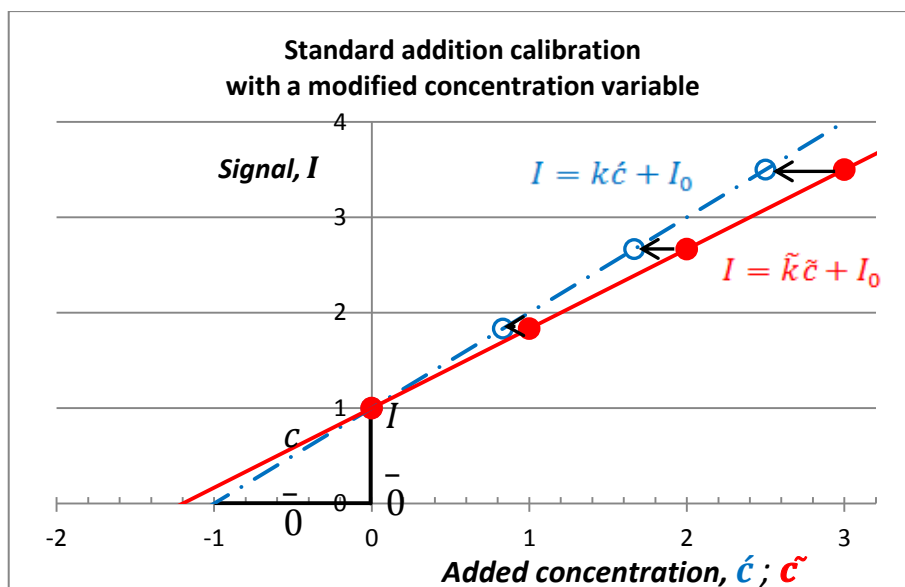


Figure 1. Standard addition with modified concentration variable, \tilde{c} , determined by known concentrations and volumes, giving the calibration line of gradient \tilde{k} . This line is directly related to the usual standard addition calibration (broken line, slope k), with added concentration variable $\tilde{c} = c - c_0$.

Screen-Printed Electrodes for Ammonia Gas Sensing in Ionic Liquids

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'Lab-on-a-chip' type designs have become increasingly popular for Amperometric Gas Sensors (AGSs) due to their portability, ease-of-use and ability to be miniaturized. Screen-printing technology is a platform for the fabrication of electrochemical sensors with those properties¹. Screen-printed electrodes (SPEs) typically consist of three electrodes (working, counter and reference) printed onto an inert substrate in a small area. The main benefits of using SPEs in AGSs are: faster response times as compared to macro or micro electrode due to the smaller volume of electrolyte needed (e.g. a thin layer), and cheaper manufacturing costs due to the smaller amount of expensive electrode material/metal (e.g. Pt or Au) required. In this work, we have employed room temperature ionic liquids (RTILs) as solvents for ammonia gas sensing on SPEs. RTILs possess several intrinsic properties such as high conductivity, high thermal stability, low volatility, high polarity, high viscosity and wide electrochemical windows². They have previously been used as a solvent for ammonia gas sensing at conventional disk electrodes³ (where NH₃ is oxidized by 3 electrons), however the electrochemical behaviour of ammonia on SPEs is unknown. This study aims to describe the electrochemical response of ammonia on SPEs to suggest if SPEs can be used for ammonia gas sensing. Recent results on voltammetry of ammonia at concentrations from 240-1360 ppm on non-modified Pt, Au and C SPE surfaces will be presented⁴. Limits of detection of 185 ppm on Au and 50 ppm on Pt are obtained using this approach, and may be further improved by modification of the working electrode surface. The results on Pt are highly encouraging and suggest that low cost SPEs can be used for ammonia gas sensing with micro-litre quantities of RTIL solvents, which may significantly reduce the costs of materials required for amperometric gas sensing devices. In addition, the unique low-volatility of RTILs may allow for more robust sensors that are able to perform in harsh conditions (such as high temperatures and pressures) where other sensor devices might fail.

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Surface Modification of Gold Coated Magnetic Nanoparticles via Electrografting of In Situ Generated Aryl Diazonium Cations

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The use of conductive gold-coated magnetic nanoparticles (MNPs) as the active element in direct electroanalytical quantification of analytes has grown recently as a result of the ability to significantly shorten the response time, decrease the detection limit and modify their surface to selectively bind to the target analyte [1, 2].

Tailoring the surface chemistry of metallic nanoparticles is generally a key step for their use in a wide range of applications. Methods to functionalize nanoparticles are generally derived from schemes used for modifying planar substrates.

In the present work, we have investigated the application of electrochemical reduction of in situ generated diazonium cations [3, 4, 5] for surface modification of gold coated MNPs. Grafting studies were undertaken using nitro benzene diazonium salt since the resulting nitrophenyl group is conveniently detected electrochemically. The behaviour of the layers formed from in situ generated diazonium salt relative to diazonium salt that was pre-synthesized prior to surface modification was also investigated.

Comparing the behaviour of the particles with gold electrode, the obtained results suggest that direct modification of particles with nitrophenyl groups can be accomplished in one step by electrochemical reduction of in situ generated nitro benzene diazonium cations generated from 4-nitro aniline. It is also found that the behaviour of the layers formed from in situ generated nitro benzene diazonium salt and the pre-synthesized nitro benzene diazonium salt is similar. Formation of the nitrophenyl layers on the surface of particles was confirmed using electrochemical conversion of the nitro moiety to the amino moiety by cyclic voltammetry (CV) [6].

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Facile synthesis of TCNQ based organic charge-transfer complexes with photocatalytic and catalytic applications

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CuTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) which is a semiconducting organic charge transfer complex and the fluoride derivative CuTCNQF₄ (tetrafluoro-tetracyanoquinodimethane) have received significant attention over the last few years due to applications in areas such as molecular based switches, field emission materials and to a lesser extent as sensing materials.^{1,2,3} However, the scope in terms of application of such materials in other technologically important areas is severely limited. It is well known that the morphology of nanostructured materials influence their properties. Therefore CuTCNQ was fabricated under significantly different conditions. The well known spontaneous reaction of Cu with TCNQ in acetonitrile was performed on a copper foil surface to form microrods but also at a highly active honeycomb Cu structure. Honeycomb copper is achieved using a hydrogen bubble templating method⁴ to create a highly porous structure with dendritic internal walls which upon conversion to CuTCNQ demonstrates a high surface coverage of very sharp needles (Figure 1). In this study new applications are presented such as photocatalysis and heterogeneous catalysis. For the former, a galvanic replacement mechanism is employed for the formation of Au-CuTCNQ nanocomposites in which the surface of CuTCNQ and their fluorinated version is partially replaced with metallic Au nanoparticles. Their photocatalytic properties are studied by the destruction of Congo red, an organic dye, by simulated solar light. The latter application was studied by reduction of 4-nitrophenol by an excess amount of NaBH₄ in the presence of CuTCNQ/TCNQF₄ at room temperature where rapid conversion to aminophenol was observed.

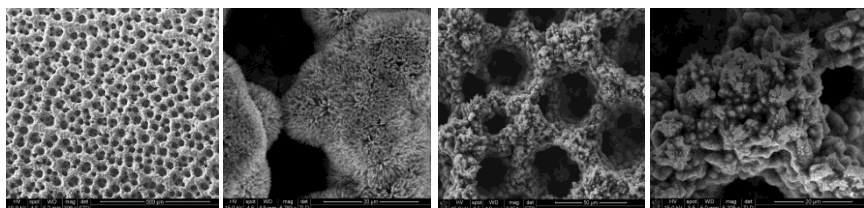


Figure 1: SEM images of (a) honeycomb CuTCNQ; (b) at higher magnification; (c) Au-CuTCNQ nanocomposites; (d) at higher magnification.

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The influence of water content on the physicochemical and electrochemical properties of ionic liquids

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Room-temperature ionic liquids (IL) can be considered one of the most promising substitutes for conventional organic solvents by virtue of their high chemical and thermal stabilities allied to essentially zero vapor pressure. Several possibilities of use as an alternative medium for many chemical processes, and their unique physicochemical properties bring up different areas to the subject, including industrial, environmental, engineering, nanomaterials and high-tech applications. Beyond the microscopic understanding of their fluidity at ambient temperatures, the step ahead is the controlling of factors that determine their properties as density, viscosity, diffusion coefficients, conductivity, etc. The many ways to chemically modify and combine different cations and anions open up an exciting field in tuning their properties according to the desired application.

The study of transport properties by addition of water to pure 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [BMMI][Tf₂N] and also with the addition of lithium salt clearly shows that the influence of water is not only on the transport properties but also on the nature of aggregates. In the case of the presence of lithium salt, the addition of water provokes an increase of the charge transport species or a diminution of the size of aggregates.

Controlled Electrocrystallization of Metals from Protic Ionic Liquids

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Ionic liquids (ILs) are salts whose melting point is below 100 °C. ILs have received much attentions as electrolytes for metal deposition due to their advantages over conventional electrolytes such as wide potential windows, thermal stability, easy in handling, non-volatile and prevention of hydrogen embrittlement [1]. ILs can be divided into two major classes, protic ILs (PILs) and aprotic ILs (AILs). PILs usually can be prepared by simple synthetic routes from reagents easily available in industry and have a relatively lower cost compared to the AILs [2]. This advantage makes PILs very suitable for industrial scale applications. There have been extensive studies on using AILs as electrolytes for electrodeposition of metals. However, study about metal deposition using PILs has not been reported so far, presumably due to the presence of proton within PILs.

In this study several PILs have been prepared and their electrochemical properties tested by using cyclic voltammetry with ferrocene/ferrocenium as the internal potential references. PILs have been used for electrodeposition of several metals onto platinum, gold and glassy carbon electrode surfaces. Various metal salts are dissolved in the PILs, and electrodeposition has been carried out at several salt concentrations. Electrodeposition of metal nanoparticles is achieved by using controlled potential mode with minimum contact with atmospheric moistures. The nucleation and growth mechanism has been detected by using chronoamperometry. The electrodeposited metal nanostructures have been characterized by using scanning electron microscopy and X-ray techniques. The dependence of the morphologies on the electrodeposition parameters such as the types of PILs, metal salts, concentration, water content, deposition potential and time has been established.

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Volumetric Interactions of Some Saccharides in Aqueous Solutions of Sodium Gluconate and Their Role in Taste Behavior

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Mechanism of taste chemoreception depends upon the water-solute interactions as well as on the compatibility of solute within water structure. So in order to understand the solute-water interactions and to get a better insight of taste chemoreception, apparent specific volumes and standard partial molar volumes of various mono-, di- and tri-saccharides have been determined in (0.25, 0.50, 1.0, and 1.5) mol·kg⁻¹ aqueous sodium gluconate solutions from precise density measurements at (288.15, 298.15, 308.15 and 318.15) K. Standard partial molar volumes of transfer, $\Delta_t V_2^\circ$ for various saccharides from water to aqueous solutions of sodium gluconate are negative and their magnitudes increase with rise of temperature, suggesting the dominance of hydrophobic-ionic interactions over the hydrophilic-ionic interactions. An attempt has been made to correlate the variation of apparent specific volumes of studied saccharides with concentration and temperature, to the basic taste quality. Volumetric interaction coefficients have been determined by using McMillan–Mayer theory. Partial molar expansion coefficients, $(\partial V_2^\circ/\partial T)_p$ and the second derivatives $(\partial^2 V_2^\circ/\partial T^2)_p$ have also been estimated. Above parameters have been rationalized in terms of solute-cosolute interactions in order to understand various mixing effects in aqueous solutions.

Performance and stability of Pd infiltrated YSZ oxygen electrodes of solid oxide electrolysis cells

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Compared with conventional water electrolysis technologies, solid oxide electrolysis cells (SOECs) can produce hydrogen at a higher chemical reaction rate less demand on electricity [1]. The performance and efficiency of an SOEC critically depends on the electrocatalytic activity and stability of the electrodes due to the development of various electrolyte film preparation technologies. Nano structured approach via infiltration is an effective method to combine the advantages of the catalytic active phases and the structural stability of the conductive porous skeleton [2].

In this work, the electrochemical activity and thermal stability of Pd infiltrated YSZ oxygen electrodes are investigated under SOEC operation conditions. The results show that the Pd infiltrated YSZ electrodes exhibit good electrocatalytic activity towards the oxygen oxidation reaction. The electrode polarization resistance of the Pd electrodes is also much lower as compared to that of the commonly used (La,Sr)MnO₃ (LSM) oxygen electrodes (Fig. 1a). On the other hand, the Pd infiltrated YSZ electrodes are not stable under the SOEC operation conditions (Fig. 1b), due to thermal instability of the Pd nanoparticles. However, the addition of a small amount of elements to form the Pd_{0.95}X_{0.05} (X=Ce, Gd, Co and Mn) alloys significantly improve the stability of the Pd electrodes (Fig. 1b). In addition, the electrocatalytic activities of these alloys are close or even better than the Pd infiltrated YSZ electrodes. The results demonstrate the nanostructured Pd infiltrated YSZ oxygen electrodes have great potential for SOEC application.

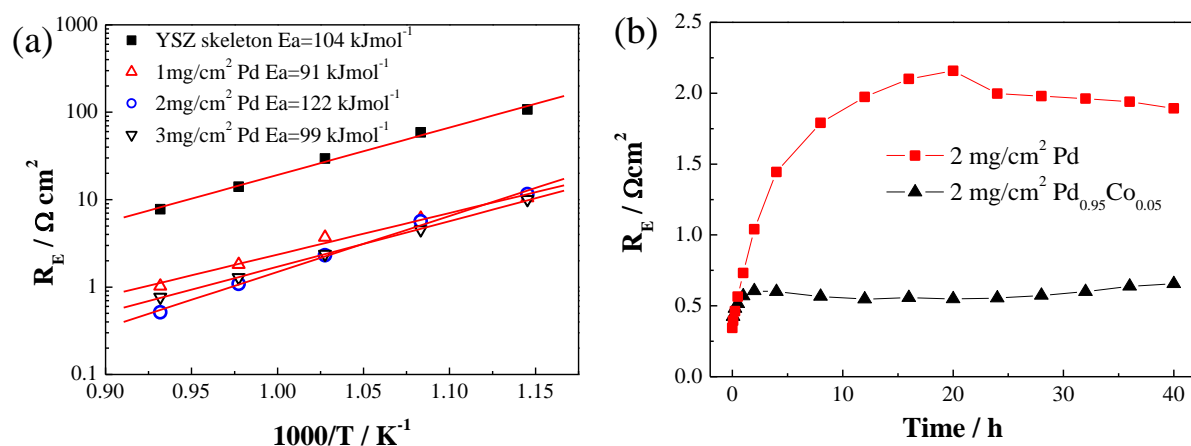


Fig. 1. (a) Plots of electrode polarization resistance (R_E) for the Pd infiltrated YSZ electrodes with different Pd loadings, and (b) changes of R_E for the Pd and Pd_{0.95}Co_{0.05} as a function of the anodic current passage at 500 mA cm⁻² and 800°C in air for 40 h.

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Characterisation of DNA modified Si(111) and Si(100) using Electrochemical Impedance Spectroscopy

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DNA sequence detection and matching has provided major benefits to a variety of fields, notably in pharmaceuticals, forensics and clinical diagnostics[1, 2]. Due to this broad applicability to various biomedical applications, there has been significant interest in the creation of smaller, faster and lower detection limit DNA biosensors to expand the scope of usability, diagnostic speed and price-points of DNA analysis and testing. Electrochemical DNA biosensors have the potential to address these goals, and the potential advantage that these devices could be made into portable systems[2]. However interfacial design is all important for DNA biosensors.

The current research aims to develop a more stable interface, allowing the sensor to become more compatible with commercial manufacturing. We have developed a novel sensing interface for a silicon-based DNA biosensor based on 'click' chemistry[3]. Amine and alkyne-modified single-stranded DNA is attached to 1,8-nonadiyne modified Si(111) and Si(100) to form the bio-recognition interface. This DNA modified surface has been characterised by Electrochemical Impedance Spectroscopy (EIS) and X-ray Photoemission Spectroscopy. Different target DNA analytes are able to be detected due to the increase in charge transfer resistance between single-stranded and double-stranded DNA.

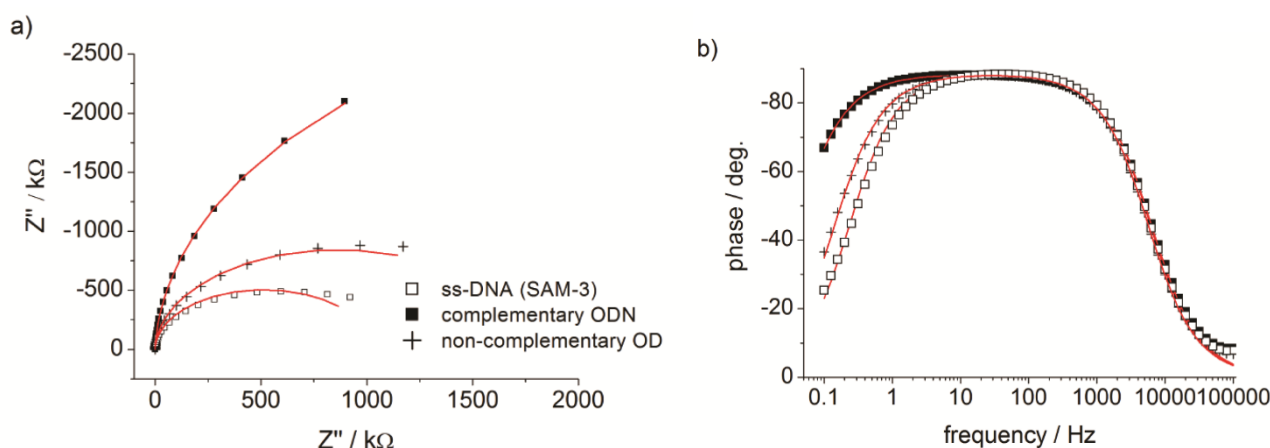


Fig. 1. Interaction of immobilized alkyne-DNA with its complementary and no-complementary strands. Complex impedance (a) and phase angle (b) plots in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for ss-DNA surface, complementary DNA and non-complementary strands. Solid lines are best fits to the data.

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New Electrochemiluminescent Horizons: Novel Platinum Schiff-base Complexes

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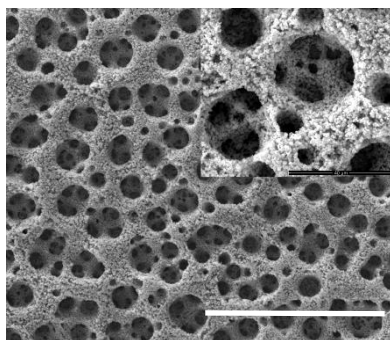
Electrochemiluminescence (ECL), the generation of light emitting states by means of electron transfer between electrochemically generated precursors continues to grow in importance as the basis for highly sensitive analytical techniques. Studies of ECL systems also provide valuable insights into the principles underpinning the operation of organic light-emitting devices (OLEDs) and light emitting electrochemical cell (LEECs) which operate under a similar mechanism. Commercial ECL systems are all based on tris(2,2'-bipyridine)ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$) or closely related derivatives. Moreover, the vast majority of research in this area has focused on ruthenium complexes of this type. This is surprising considering the relatively low luminescent quantum yields and limited wavelength tuneability of such complexes, (eg. $[\text{Ru}(\text{bpy})_3]^{2+}$ shows only ~4% quantum efficiency in aqueous media). New materials possessing tuneable emission wavelengths and higher quantum efficiencies would significantly enhance the sensitivity and selectivity of current ECL detection systems. The broad objective of the work is to discover new ECL luminophores outside the realm of ruthenium, evaluate their properties and suggest new avenues of exploration for ECL systems.

A series of platinum (II) complexes with Schiff base ligands were synthesized and compared in search for better luminophores for electrochemiluminescent (ECL) based sensing applications. We demonstrate the ability to tune the energetics of the reaction leading to the emitting state, tune the energy of the excited state itself and most importantly, increase our understanding of these systems and their potential for ECL application. A range of photophysical and electrochemical techniques have been used to explore the relationship between the photophysical and redox properties of the new transition metal complexes. The findings provide insights into the characteristics required for efficient ECL and suggest new directions in the search for novel ECL luminophores.

Rapid electrochemical synthesis of highly active Cu/Pd and Cu/Au bimetallic honeycomb films

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A rapid synthesis of continuous bimetallic honeycomb films has been investigated via electrochemical deposition in the presence of hydrogen evolution by the so called hydrogen bubble templating route.^{1,2} A significant advantage of this approach is that the template is both clean and transitory. Two metal systems (Cu/Pd and Cu/Au) have been investigated and co-deposited on various substrates (Cu, Pd, Au) with noticeable structural variations between the different substrates. This is manifested in terms of different pore size, distribution and interconnectivity of the overall honeycomb structure. The honeycomb films are highly porous with pore sizes in the micrometer range while also demonstrating nanoscale porosity within the internal wall structure. A typical example of a Cu/Pd honeycomb film is shown below.³ Significantly, we are able to show that the pore size and their distribution together with structural depth can be fine-tuned by varying parameters such as the metal salt to acid ratio, ratio of the two precursor metal salts, deposition time and the nature of the substrate. Owing to the large surface area and evidence of alloy formation in both the bulk and surface of the bimetallic porous structures, they display enhanced heterogeneous catalytic and electrocatalytic properties together with increased SERS sensitivity and resolution.



Typical SEM image of a Cu/Pd bimetallic foam structure. Scale bar is 200 μm .

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Modified Electrodes for Detecting Bacterial Activity

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Electron transport chain is fundamental to the respiratory process in the mitochondria of all higher animals and plants. The respiratory process initially involves an enzyme-initiated breakdown of glucose and other substrates. The process results in the transfer of electrons from the substrate to redox co-factors such as NADH. The electrons are subsequently transferred through a series of several similar redox cofactors bound to integral membrane or membrane-associated protein complexes. The process terminates in the transfer of electrons to high-redox-potential electron acceptor such as oxygen. The free energy from the electron transport chain generates proton motive force, which subsequently drives the synthesis of ATP.¹ Interestingly, bacteria and several other microbes possess a complex electron transport chain, capable of transferring electrons to a range of extracellular electron acceptors ranging from Fe^{3+} , NO_3^- , halogenated hydrocarbons and several membrane permeable redox active molecules such as thionine, benzylviologen, phenazines, phenothiazines, iron chelates, quinones etc. Such extracellular electron transfers have found interesting applications such as reductive transformation of halogenated hydrocarbons, degradation of azo dyes and construction of microbial fuel cells.² In our study, we aim to construct modified electrodes to probe and understand the mechanism of such extra cellular electron transfers in bacteria, with the view for better implementation of reductive transformation of halogenated hydrocarbons.

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New Dimensions in Electrochemiluminescence

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In recent times Electrochemiluminescence (ECL) has emerged as an important analytical technique, its selectivity and sensitivity making it suitable for the detection of a wide range of compounds. ECL as a technique is exploited routinely in commercial applications for rapid, sensitive detection and quantification of biomarkers, food borne pathogens and biowarfare agents. New applications of ECL as a sensing technique continue to appear in a wide range of fields, with new ECL active luminophores having diverse properties being developed. Generally a single luminophore is excited in an ECL experiment without wavelength discrimination, for example tris(2,2'-bipyridyl)ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$) emits strong co-reactant ECL centered at 620 nm.

This work explores the use of multiple, selectively excited ECL luminophores in a single solution. The emitting species of interest have been developed to have complimentary photophysical and electrochemical properties, and can thus be selectively excited via application of different electrode potentials, while emission from each luminophore can be independently quantified using a wavelength-sensitive detector such as a CCD.

We have developed a new instrumental approach, combining rapid acquisition of spectral data synchronised with electrochemical experiments that enables rapid characterization of these luminescent redox systems by simultaneous representation on the potential/time and the wavelength axes. This 3D approach to ECL will open up potential new applications in multiplexed ECL detection and color selection in light-emitting devices as well as providing fundamental insights into interdependent electrochemical and spectroscopic properties and energy transfer mechanisms.

Characterization of Electrochemically Roughened Platinum Electrode: Exposure to the Atmosphere

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The design of next-generation high-resolution and site-specific neural prostheses requires greater numbers of microelectrodes. However for a fixed charge, reduction in electrode size increases charge density. If charge density exceeds the reversible charge injection limit, undesirable and irreversible electrochemical reactions occur which damage both stimulating electrodes and neural tissues. An effective way to increase the charge injection limit and maintain low impedance of electrodes is to increase the surface roughness.

Electrochemically roughened (HiQ) Pt electrodes with high real surface area (~75 times greater) than standard Pt electrode of same geometric size, showed low polarization, impedance and residual direct current [1,2]. However HiQ Pt electrodes lose effectiveness when exposed to atmosphere but maintain their effectiveness when stored in water. In this work we want to present preliminary results correlating electrochemical behaviour of roughened electrode with their surface chemical composition and morphology after exposure to different environments. The real surface area, polarization and impedance of HiQ electrodes were measured after exposing to various environments. XPS was used to examine chemical composition at the surface. The surface morphology was studied by AFM and SEM.

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Electrochemical DNA Sensor for Ultrasensitive DNA Sequence Specific Detection of *Legionella* sp. and Dengue

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Electrochemical DNA sensors have attracted considerable attention because of simple instrumentation, low cost, portability, fast response time, high specificity, sensitivity and low limit of detection. Limit of detection can be significantly improved by employing either redox recycling in which two redox species are coupled to achieve electrochemical signal amplification or fabricating the electrode substrate into nanoporous multi channel structure for probe immobilization. Amplified electrochemical DNA sensor is constructed using thiolated hairpin DNA-ferrocene probes on gold electrode. The switching from “on” to “off” states of individual probes in the presence of complementary DNA target influences the electrode potential, besides the current, owing to changes in surface density of the electroactive hairpin DNA-ferrocene probes. Electrochemical nanoporous alumina electrode based DNA biosensor is constructed by immobilizing aminated probe DNA in the alumina nano channels and binding of target complementary DNA to probe inside nanochannels causes changes in mass transfer of redox species $\text{Fe}(\text{CN})_6^{4-}$ through the nanochannels. The changes in mass transfer of redox species through the alumina nanopores are translated into electrochemical signal using differential pulse voltammetric technique. The biosensors demonstrate linear range over 8-9 orders of magnitude with ultrasensitive detection limits for the quantification of a 21-mer and 31-mer DNA sequence. Its applicability is tested against PCR amplicons derived from genomic DNA of live *Legionella pneumophila* and Dengue viruses. Excellent specificity down to one and three nucleotides mismatches in another strain of different species, respectively, is also achieved.

Self-Powering Amperometric Sensor and Biosensor

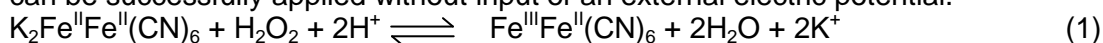
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Abstract

We prepared and developed a self-powering sensor and biosensor for the detection of hydrogen peroxide and glucose based on a porous Prussian blue nanotube (PB-*nt*) membrane electrode. It is well known the Prussian blue has a high catalytic activity for the reduction of hydrogen peroxide and is itself reduced by electron flow from the counter reaction at the auxiliary electrode as shown in Eq. 1 [1-3]. As the porous Prussian blue nanotube membrane serves as working electrode and separates a sensing solution from the reference solution which contains the reference and auxiliary electrodes, the design of self-powered biosensors based on Prussian blue nanotube with using a two-compartment cell derives the current signal from the chemical energy of the hydrogen peroxide analyte. The sensor can be successfully applied without input of an external electric potential.



The potential controlled voltammetric experiments and measurements of the sensor electrochemical potentials indicate the PB-*nt* are of similar characteristics as usual PB films and that the sensing reaction proceeds via reduction of hydrogen peroxide. Excellent curve fits of the potential and current data to theory indicates the spontaneous reduction of hydrogen peroxide at the PB-*nt* together with the Galvanic cell regeneration of the reduced form of PB, proceeds under steady-state condition. Outstanding analytical performance of the self-powering sensor towards hydrogen peroxide is comparable to potential-controlled PB sensors. This strategy also gives low detection limit of 0.1 μM H_2O_2 with linear range up to 80 μM .

Glucose biosensor derived from the hydrogen peroxide sensor is further demonstrated in the presence of a homogeneous solution of glucose oxidase enzyme, indicates the possibility for other oxidase enzyme-based biosensors. This concept is presently applied to prepare virus specific biosensor.

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Effect of anodization conditions on the formation of low-aspect-ratio tantalum oxide nanotubes

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Previous work in our group with glucose biosensors, employing the enzyme Glucose Oxidase (GOx) and Ir oxide (IrOx) nanoparticles (1), has shown a highly sensitive response to glucose, involving fast electron transfer between these two materials. Additionally, these sensors exhibit a glucose response in aerated or deaerated conditions and good selectivity for glucose. However, poor reproducibility between sensors reveals the need for increased structural control of the sensor components. In parallel work, our group has been investigating the formation of high aspect ratio Ta oxide (Ta_2O_5) nanotubes (NTs) of 1 to 15 μm in length (2). Ta_2O_5 exhibits preferential qualities, such as biocompatibility, and chemical and mechanical stability, making it a suitable material for biological applications. Therefore, the long-term goal of this work is to optimize the nano-structuring of our GOx/IrOx-based glucose sensor by employing Ta_2O_5 NTs as a deposition template.

For this application, much shorter NTs are required than have been previously developed (2), allowing easier deposition of GOx and IrOx and creating a relatively short diffusion pathway for glucose and its product, gluconic acid, leading to higher sensitivity, better sensor correlation to blood glucose levels, and shorter sensor lag times. Therefore, a reliable method of precisely controlling NT length during formation has been developed. The Ta_2O_5 NTs were prepared by Ta anodization in a solution containing HF, H_2SO_4 and H_2O in a two-electrode cell configuration. Using the anodization conditions previously reported, NTs of ca. 1 μm in length were formed after 20 seconds of anodization (2). To decrease the NT growth rate, the concentration of HF was reduced to 5-30% of the initial concentration, thus allowing for precise control of NT length during formation. NT length was determined by cross-sectional FE-SEM imaging, showing a good correspondence with lengths calculated, based on a proposed mechanism of NT formation. The NT length was then correlated to the charge passed during anodization to create a calibration curve, which allows for accurate prediction and tuning of NT length during anodization.

Upon lowering of the HF concentration, a thin film with excellent adhesion and uniform thickness (ca. 10 nm) is observed to lie on the outer surface of the NTs. This film, although porous, may restrict the deposition of metals and enzymes and limit the diffusion of analytes and products in and out of the NTs. Surface characterization methods, such as x-ray photoelectron spectroscopy and Auger electron spectroscopy, are currently being used to determine the composition and origin of this potentially blocking surface film. Alternative anodization conditions to avoid the formation of this film are also being investigated.

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Electrochemically Directed Synthesis and Properties of Structurally Characterized $[\text{TTF}]_4[\text{SVM}_{11}\text{O}_{40}]$ ($\text{M} = \text{Mo}, \text{W}$; TTF = tetrathiafulvalene) Charge Transfer Materials

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The first reported organic metal TTF-TCNQ (TCNQ = tetracyanoquinodimethane) complex was discovered in 1973. The fact that reaction of TTF with TCNQ is rapid facilitates studies of interfacial chemistry between the two solids. Recently the metallic conductivity was obtained at the interface between insulating TTF and TCNQ crystals that are in direct mechanical contact, which in turn generated a new direction of interest in the study of interfacial phenomena in charge-transfer complexes.

Following the discovery of the metallic TTF-TCNQ complex, other charge-transfer complexes derived from TTF were synthesized and have turned out to exhibit properties associated with semiconductors, metals and even superconductors. Polyoxometalate (POM) anions, due to their rich redox chemistry, electronic versatility, magnetism and photochemistry, are attractive candidates to form hybrid bifunctional materials containing POM anions and TTF. Most commonly, TTF-POM complexes have been synthesized by electrocrystallization. However, in principle, if the POM anions can be set up appropriately, TTF-POM complexes should become available by spontaneous reaction of TTF and POM, analogously to the reaction between TTF and TCNQ. In this study, the redox features of vanadium-substituted Keggin-type polyoxometalates $[\text{n-Bu}_4\text{N}]_3[\text{SVM}_{11}\text{O}_{40}]$ ($\text{M} = \text{Mo}, \text{W}$) and TTF allow the synthesis of charge-transfer complexes $\text{TTF-SVMo}_{11}\text{O}_{40}$ and $\text{TTF-SVW}_{11}\text{O}_{40}$ by rapid spontaneous reactions in solid state or solution phase between TTF and $[\text{n-Bu}_4\text{N}]_3[\text{SVM}_{11}\text{O}_{40}]$ ($\text{M} = \text{Mo}, \text{W}$). A stoichiometry of $[\text{TTF}]_4[\text{SVM}_{11}\text{O}_{40}] \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_2\text{Cl}_2$ was given by single crystal X-ray crystallographic analysis. Raman spectra, elemental analysis and voltametric data are consistent with the oxidized TTF charge state and the formulation deduced by crystallography. A rod type morphology of the new charge-transfer molecule $\text{TTF-SV}^{\text{IV}}\text{Mo}_{11}\text{O}_{40}$ was demonstrated by SEM images, while the $\text{TTF-SV}^{\text{IV}}\text{W}_{11}\text{O}_{40}$ material exhibited a diamond-like morphology. The conductivity at room temperature is in the semiconducting range. EPR spectra confirm the presence of paramagnetic V (IV) and paramagnetic oxidized TTF and show that the $\text{TTF-SV}^{\text{IV}}\text{M}_{11}\text{O}_{40}$ complexes prepared from either solution phase or solid state reaction are spectroscopically equivalent. The newly isolated $\text{TTF-SV}^{\text{IV}}\text{M}_{11}\text{O}_{40}$ complexes having dual electrical and magnetic functionality represent a new class of TTF-polyoxometalate compounds.