



ISE Satellite Student Regional Symposium on Electrochemistry

20th Australian/New Zealand Electrochemistry Symposium (20ANZES)

Sunday 17th April 2016

University of Auckland, New Zealand

Electrochemistry Division – Royal Australian Chemical Institute

New Zealand Institute of Chemistry

Programme with Abstracts



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<i>Welcome</i>	<i>8:50</i>	Title
Invited: Prof. Richard McCreery	9:00 – 9:35	Modified Electrodes in Solid-State Electronic Devices
<i>Chair: Alissa Hackett</i>		
Anna Farquhar	9:35 – 9:50	Modifying Free-Floating, Few-Layer Graphene Sheets via the Spontaneous Reaction of Nitrobenzene Diazonium Ions
Yang Liu	9:50 – 10:05	Visualisation of Diffusion Processes within Nanopore Arrays
Eva Alvarez de Eulate	10:05 – 10:20	Liquid-liquid interfaces supported by laser-ablated glass micro-pore membranes for electrochemical analysis
	10:20-11:00	<i>Morning tea/posters</i>
Bond Medal: Dr. Leigh Aldous	11:00 – 11:25	Electrolyte-driven focus on electrochemical methods of harvesting waste energy
<i>Chair: Eva Alvarez de Eulate</i>		
Ghulam Hussain	11:25 – 11:40	Low-Concentration Detection of Ammonia Gas on Miniaturised Electrodes in Room Temperature Ionic Liquids
Jacqui Delaney	11:40 – 11:55	Mobile Phone Based Sensing with Transparent Electrodes for Enhanced Electrochemiluminescence Sensitivity
Colin Kang	11:55 – 12:10	The Electrochemical Behaviour of Trinitrotoluene (TNT) Reduction in Room Temperature Ionic Liquids (RTILs)
	12:15 – 1:15	<i>Lunch/posters</i>

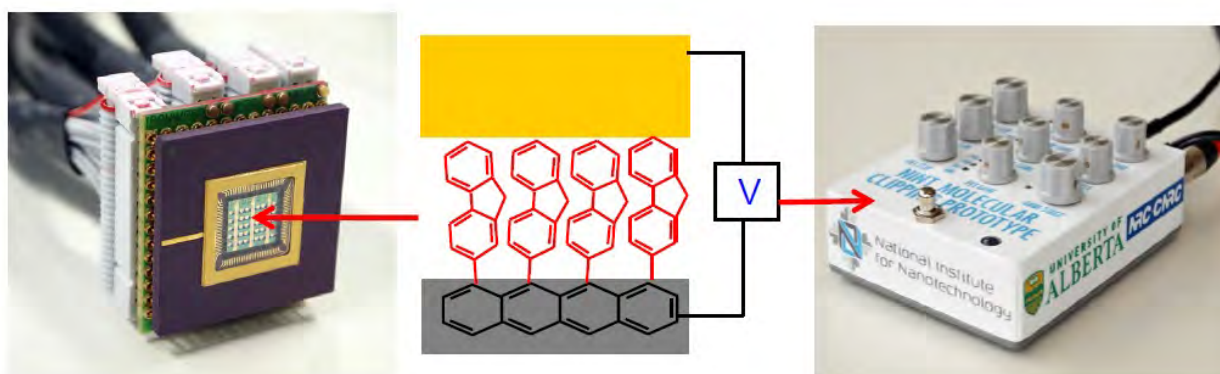
Invited: Prof. Ulrich Stimming	1:15 – 1:50	Model Catalysts and Biological Molecules Investigated by Scanning Probe Microscopies
<i>Chair: Brad Stringer</i>		
Md Abu Sayeed	1:50 – 2:05	Investigation of the applicability of amorphous Co(OH) ₂ on a gold support for electrochemical water splitting and glucose sensing
Tobias Baldhoff	2:05 – 2:20	Electrochemical Impedance Study of Oxide Films Formed During Electropolishing of Aluminium in Phosphoric Acid
Alissa Hackett	2:20 – 2:35	Conductive surfaces responsive to temperature and salt
	2:35 – 3:15	<i>Afternoon tea/posters</i>
<i>Chair: Md Abu Sayeed</i>		
Ruchika Ojha	3:15 – 3:30	EPR spectroscopic characterisation and fate of a monomeric Pt ^{III} species produced via electrochemical oxidation of anticancer compound <i>trans</i> -[Pt ^{II} {(<i>p</i> -BrC ₆ F ₄)NCH ₂ CH ₂ NEt ₂ }Cl(py)]
M A Haghighatbin	3:30- 3:45	Spectroscopic, electrochemical and electrochemiluminescent properties of highly luminescent iridium(III) 1,2,4-triazole complexes
Bradley Stringer	3:45 – 4:00	Electrochemiluminescent energy transfer between d-metal donors and f-block lanthanide acceptors

ORAL PRESENTATIONS

Modified Electrodes in Solid-State Electronic Devices

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Molecules may be considered electronic systems, with electrons rapidly moving through molecular orbitals and also long distances in biological metabolism and photosynthesis. The prospect of incorporating molecules into microelectronic circuits based on silicon and metallic conductors has great potential for enhancing consumer electronics, providing solar energy conversion, and permitting new functions not possible with silicon. In order to combine the electronic properties of molecules with conventional microelectronics, we need to understand how to “connect” to molecules as well as how electrons are transported through molecules. Once the “rules” of charge transport through molecules are understood, it should be possible to “rationally design” new molecular electronic devices for valuable functions not currently possible with silicon. While Molecular Electronics holds great promise, it also presents significant challenges in handling and fabrication of devices with dimensions of only a few nanometers. We use surface chemistry, spectroscopy, and conjugated organic molecules to make “molecular junctions” consisting of a single layer of molecules between conducting carbon and copper electrodes, then we study the behavior of molecules as circuit elements. The primary goal is to design and build functional molecular electronic components to greatly enhance the already powerful world of silicon microelectronics. A demonstration of the first commercial application of molecular electronics in audio processing will be presented.



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Modifying Free-Floating, Few-Layer Graphene Sheets via the Spontaneous Reaction of Nitrobenzene Diazonium Ions

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Few-layer graphene (FLG) is predicted to have numerous applications due to its impressive array of chemical and mechanical properties,¹ such as a large surface area, high electrical conductivity, and good optical transparency.² In order to exploit these properties, it is first necessary to covalently functionalise the graphene sheets. This work explores the modification of free-floating graphene sheets on an aqueous solution of a nitrobenzene diazonium salt. This modification strategy eliminates commonly seen substrate-induced effects.³ A novel protocol for functionalisation and subsequent characterisation has been developed (Figure 1A), which allows multiple analysis techniques to be used on a single sheet of graphene.

The modified surfaces were examined using atomic force microscopy, X-ray photoelectron, infrared and Raman spectroscopy, and electrochemistry. The results demonstrate that at least two reaction pathways are involved for spontaneous film growth: the typical radical based mechanism giving a -C-C- linkage, and a direct reaction of the diazonium cation with the surface forming a -N=N- linkage. This is shown by infrared and X-ray photoelectron spectroscopy. In this study the modified graphene was mounted onto HOPG for electrochemical and atomic force microscopy analysis in either an "exposed" or "sandwiched orientation (Figure 1B). In the "sandwiched" orientation an additional nitro reduction peak can be seen. This is the first evidence for such a peak, and it is suggested that it is a result of the different reduction potentials of the nitro groups at graphene and HOPG. It can only be seen when groups are "sandwiched" between these two surfaces. Also, in the "sandwiched" array, the measured surface concentration is significantly higher than previously reported concentrations and those measured for the "exposed" orientation. This is due to the ability to access more of the multilayer film because electrons can be transferred from both the graphene and HOPG surfaces.

This work fully investigates the film structure of a nitrobenzene diazonium modified graphene sheet. It also provides insight into the electrochemical properties of such systems.

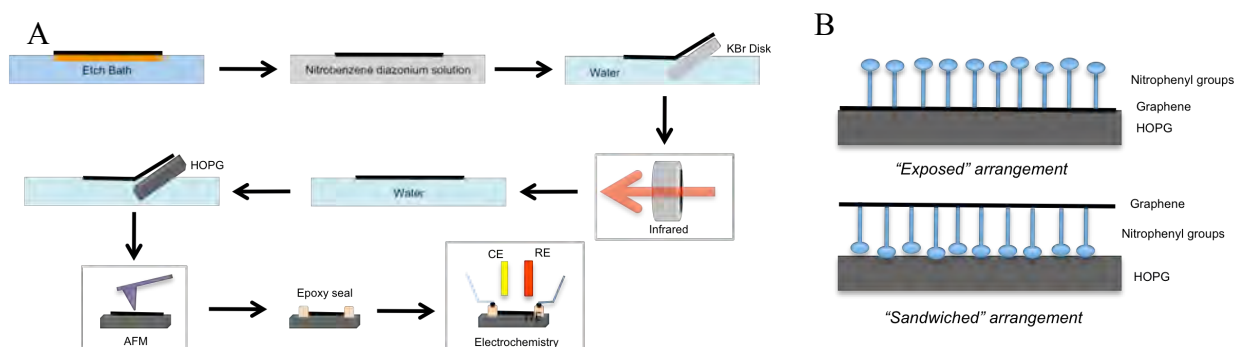


Figure 1: (A) Novel protocol for the modification and subsequent analysis of free-floating, few-layer graphene; (B) "Exposed" vs. "sandwiched" arrangement for electrochemistry

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3. Wang, Q. H.; Jin, Z.; Kim, K. K.; Hilmer, A. J.; Paulus, G. L. C.; Shih, C.-J.; Ham, M.-H.; Sanchez-Yamagishi, J. D.; Watanabe, K.; Taniguchi, T.; Kong, J.; Jarillo-Herrero, P.; Strano, M. S. Understanding and Controlling the Substrate Effect on Graphene Electron-Transfer Chemistry Via Reactivity Imprint Lithography. *Nat Chem* **2012**, 4, 724-732.

Visualisation of Diffusion Processes within Nanopore Arrays

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Diffusion of chemical species through and from nanopores and nanochannels is essential in many fields, such as single DNA molecule analysis and the transport of ions of biological interest through membrane channels. A better understanding of mass transport behaviour at nanopores and nanopore arrays will enable a more efficient design of nanodevices that rely on parallel measurements in liquid. Although computational simulation methods provide a basis for the study of diffusion at nanoarrays, the development of experimental visualisation approaches is highly desirable to provide straightforward evidence of the behaviour occurring at such small electrochemical systems. However, this remains challenging owing to a lack of effective tools.

In this work, experimental methods to visualise such diffusion were examined. First, two regular nanopore arrays with different ratios of pore center-to-center distance (r_c) to pore radius (r_a) were fabricated by focused ion beam (FIB) milling of silicon nitride (SiN) membranes (Figure 1A). The deposition of silica on the nanointerfaces between two immiscible electrolyte solutions (nanolTIES) supported by these arrays were achieved based on the diffusion of surfactant ion, transferred from organic to aqueous phase, as the template. It was found that r_c/r_a had a significant impact on diffusion within the array of nanopores ($r_a = 86 \pm 6$). The silica material modified the entire array at the closer-spaced pores (Figure 1Ba, $r_c/r_a = 21 \pm 2$), while individual pore modification by silica was observed at the widely spaced pores (Figure 1Bb, $r_c/r_a = 91 \pm 7$). This is attributed to the formation of overlapping diffusion zones at arrays with $r_c/r_a = 21 \pm 2$ or individual diffusion zones at the pores of the array with $r_c/r_a = 91 \pm 7$, respectively (Figure 1C, a & b). Imaging of the topography and diffusion of a redox species through these nanopore arrays was also achieved by combined atomic force - scanning electrochemical microscopy (AFM-SECM), providing further confirmation of the different diffusion behaviours. These new methods enable direct visualisation and understanding of mass transport at the nanoscale, which opens up new opportunities for the development of highly efficient nanosystems.

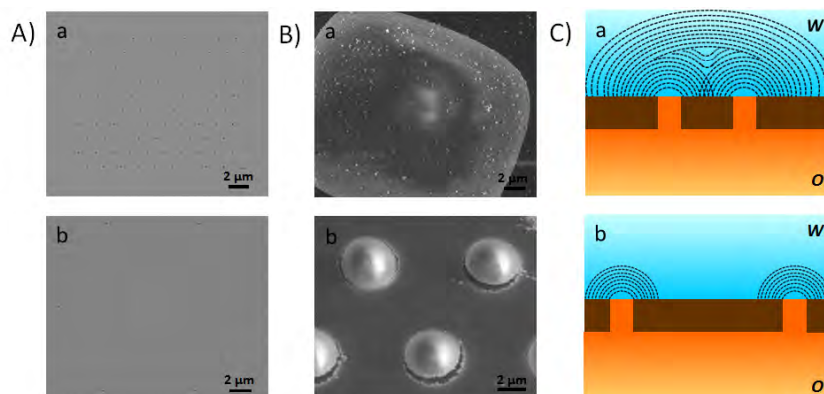


Figure 1. SEM images of the nanopore arrays with r_c/r_a of 21 ± 2 (a) and 91 ± 7 (b) before A) and after modification of silica materials B). C) Schematic views of their interfacial diffusion profiles.

Liquid-liquid interfaces supported by laser-ablated glass micro-pore membranes for electrochemical analysis

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) has been used to study charge transfer processes at organic-aqueous interfaces, with benefits to chemical sensing in terms of non-redox detection of ionisable analytes. Miniaturisation of the ITIES to microscale brings the advantage of enhanced mass transport, and arrays of microscale interfaces enable the current signal to be amplified by the number of elements in the array. To date, silicon, silicon nitride or organic polymeric substrates have been used to form micro/nano-ITIES arrays; however glass has been used only in the form of pulled glass pipettes.

In this work, arrays of micropores in glass membranes were evaluated as platforms for the formation of μ ITIES arrays. This was achieved by laser ablation of 10 x 10 square arrays in $\sim 130\ \mu\text{m}$ thick borosilicate glass coverslips (Fig. 1A). The laser entry side presented pore diameters of ca. $50\ \mu\text{m}$ and the exit side ca. $25\ \mu\text{m}$. The glass surface was selectively coated on one side and on the pore inner walls with a fluorinated silane (Fig. 1B) to support the formation of stable organic-aqueous interfaces. The ion transfer of tetrapropylammonium (TPrA^+) across the water/1,6-dichlorohexane micro-interface array was investigated experimentally together with finite element computational simulations using interfaces formed at either the laser entry side or the laser exit side (Fig. 1C). The experimental and simulation data suggest that the smallest micro-interfaces (laser exit side) were located at the pore mouths in hemispherical geometry, whilst the larger micro-interfaces (laser entry side) were flatter in shape but exhibited more instability due to the roughness of the glass around the pore mouths. Also, the equi-concentration lines in the diffusion profiles obtained via simulation indicate a small deviation from purely spherical diffusion fields, particularly the smaller ratio pore-to-pore separation / pore radius ($r_c / r_a \sim 12$) configuration. The work presented here provides a new platform for chemical and biochemical sensing via electrochemistry at the ITIES with the advantages of a simple fabrication process, well-known glass surface chemistry and the possibility to combine with optical methods.

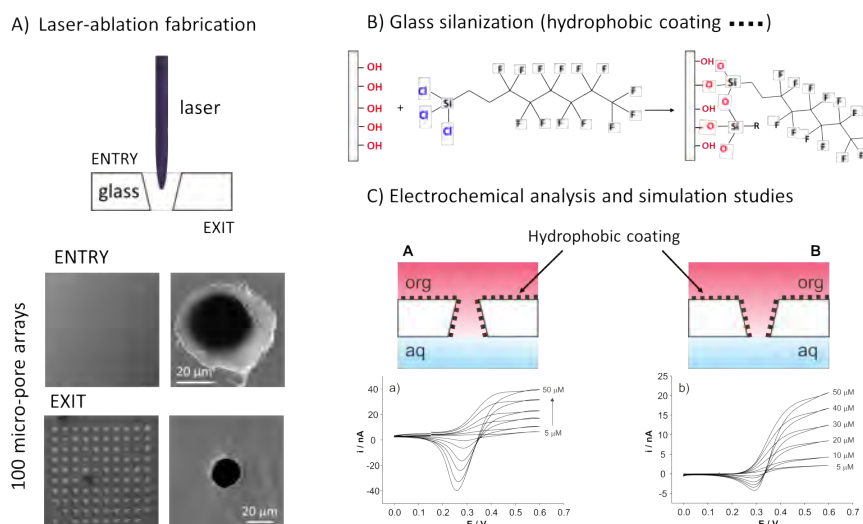


Figure 1. A) Sketch of the membrane fabrication and SEM images of the μ -pore array, B) silanization reaction to coat the glass membrane and C) voltammograms obtained for TPrA^+ transfer across water/1,6-dichlorohexane μ -interfaces formed with the different configurations of the glass μ -array.

Electrolyte-driven focus on electrochemical methods of harvesting waste energy

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This talk will describe some recent research performed in the Aldous group focusing upon the role of the electrolyte in novel routes aimed at turning waste into value added products, namely electricity and feedstock chemicals. The electrochemical techniques used will focus upon biomass-fuelled air-batteries (where the 'exhausted fuel' is ideally value added chemicals), and thermoelectrochemistry (for harvesting waste heat into an electrical current).

Ionic liquids have left electrochemists spoilt for choice in terms of 'designer' electrolytes. A particularly exciting aspect is their ability to dissolve significant quantities of biomass, under relatively mild conditions.[1] The deliberate burning biomass to release its energy actually outdates modern humans, and has likely been practiced for more than a million years already.[2] Due to our relatively recent ability to dissolve biomass, we can now scope to access this enthalpic energy by 'electrochemical combustion', using dissolved biomass as a fuel in air-batteries or direct fuel cells. Our recent progress in this area will be summarised.

Thermal energy is also wasted on a massive scale. Electrochemistry can be used to prepare 'entropy batteries', which can convert a temperature difference into an electrical current using an appropriate redox couple.[3] In this case, the electrolyte also has a key role to play. Recent research has focused upon evaluating electrolytes for their thermoelectrochemistry, in particular when the electrolyte, solvent and redox couple are all the same thing (*i.e.* a redox-active ionic liquid).

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Low-Concentration Detection of Ammonia Gas on Miniaturised Electrodes in Room Temperature Ionic Liquids

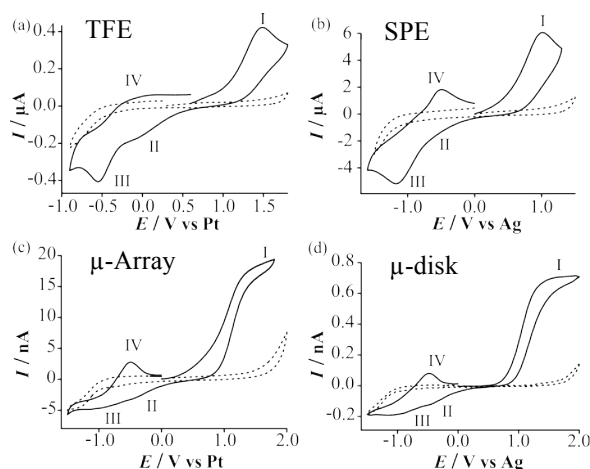
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Low concentration ammonia (NH_3) gas detection is of great importance due to its wide use in a range of industries i.e. mining industry, fertilizer industry, oil and gas industry, refrigeration industry¹ and due to its high toxicity. Concentrations as low as 500 ppm can be lethal, and the current (USA) Occupational Health and Safety Permissible Exposure Limit (OSHA PEL) for ammonia is 25 ppm in the gas phase. Amperometric gas sensors (AGSs) are commercially available to monitor ammonia gas. However there is one problem with AGSs are their solvent/electrolyte combinations which are typically water/sulphuric acid or conventional organic solvent/supporting electrolyte, and can dry-up quickly, thus making the lifetime of these sensors very limited. Room Temperature Ionic Liquids (RTILs) have been attracting a great attention² as replacement electrolytes in AGSs due to their unique physical properties such as low volatility and negligible vapor pressure, wide electrochemical windows, high ionic conductivity, and their better ability to dissolve a wide range of organic and inorganic compounds. Importantly, they do not evaporate when exposed to a high gas flow, and can function in harsh conditions such as hot and dry environments. In our work, we are investigating new commercially available thin-film metal electrodes, which typically consist of three electrodes that are incorporated onto a small area on an inert substrate. Their small size means that only a few microliters RTIL solvent needed, and the small amount of inert metal required (e.g. platinum) which minimizes the overall cost of the sensor. A comparison of four different electrochemical techniques will be employed for ammonia gas oxidation: linear sweep voltammetry (LSV), potential-step chronoamperometry (PSC), differential pulse voltammetry (DPV) and square wave voltammetry (SWV), over the concentration range of 10-100 ppm NH_3 . The results on commercially available Pt thin-film electrodes (TFE), screen-printed electrodes (SPE), and microarray thin-film electrodes (μ -Array) will be compared to "ideal" home-made Pt microdisk electrodes (μ -disk). Calibration graphs (current vs. concentration) for all voltammetric techniques on all four surfaces will be presented, showing excellent linearity with increased concentrations of NH_3 . The limits of detection found on all four surfaces for all four techniques are in the range of ca. 2-5 ppm, much lower than minimum exposure limit (25 ppm) for NH_3 . These results are highly encouraging and suggest that RTILs and low-cost miniaturised electrodes can be combined in sensor devices to detect ammonia gas at low concentrations.

References:

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Cyclic voltammetry of 500 ppm ammonia on four Pt surfaces in the RTIL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{C}_2\text{mim}][\text{NTf}_2]$). Dotted line is blank voltammogram without ammonia. Scan rate 100 mVs^{-1} .

Mobile Phone Based Sensing with Transparent Electrodes for Enhanced Electrochemiluminescence Sensitivity

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There has been a substantial interest from researchers in producing low-cost sensors for applications in the developing world. In the development of low-cost sensors, keeping costs minimal is one of the most important aspects. Apart from using cheaper materials and fabrication techniques, another approach to keeping costs down, is to use an extant ubiquitous device such as a mobile phone as the detector. Most such work reported to date has focused on exploiting the built-in camera for colorimetric detection. Colorimetric detection with a mobile phone however suffers from dependence on ambient light, which adversely affects reproducibility, especially for field use. We recently reported the use of a mobile phone to initiate, detect and analyse an electrochemiluminescent (ECL) reaction [1].

Detection with a mobile phone is attractive not only because of the reduction in cost, but also because of the opportunities for telemedicine it affords. ECL is advantageous over colorimetric detection because it is completely independent of ambient light. Other methods of detection include electrochemical, however electrochemical detection requires extra instrumentation. As we have shown, not only can ECL be captured and analysed with a mobile phone, but the electrochemical excitation necessary to initiate the ECL emission can also be provided by such a device [1]. The results obtained were an acceptable starting point for proof-of-concept, however it was believed that the sensitivity could be improved upon by using transparent electrodes.

In this presentation we will illustrate an approach to enhance the sensitivity of ECL mobile phone detection by using a transparent electrode as the sensor substrate. Previously a screen printed electrode was used, however there was a loss of photons in the paper leading to a decrease in sensitivity. We will show that by using transparent electrodes the detection can be performed from the back of the sensor meaning the photons no longer get attenuated by the paper. This leads to an increase in sensitivity making the idea of ECL mobile phone detection a real possibility.

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The Electrochemical Behaviour of Trinitrotoluene (TNT) Reduction in Room Temperature Ionic Liquids (RTILs)

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The detection of TNT is of utmost importance due to its phenomenal power and capability to cause immense destruction and malicious injury to living beings. There are several methods that are used for explosives detection but these methods are not always as portable or low-cost as electrochemical sensors. Thin film electrodes (TFEs) are a new type of miniaturised sensing surface where the working, counter and reference electrodes are printed on a planar substrate, exhibiting portable capabilities. Both a conventional microelectrode and thin film electrodes were utilised to investigate the electrochemical behaviour of TNT in eight different RTILs. The benefits of using RTILs as the solvent are their non-volatile properties and high thermal stability¹ – ideal for explosives sensing especially in hot and dry environments. In this work, three reduction peaks were observed in voltammetry in all eight RTILs, likely corresponding to the reduction processes of each one of the three nitro groups on TNT. Electrochemical studies determined that for all RTILs, reduction peak I was likely to be chemically reversible whereas peak II and III were likely to be chemically irreversible. In addition, it was found that the electrochemical behaviour of TNT can vary, depending on the RTIL employed (resistive behaviour, broadened peaks, potential differences etc.). Potential-step chronoamperometry was conducted to calculate diffusion coefficients of TNT in RTILs, reportedly for the first time. Furthermore, TNT was observed to behave in accordance with the Stokes-Einstein relationship, associated with diffusional behaviour of a ‘stick’ mechanism. The electrochemical reduction mechanism of TNT was found to occur via an EC₂ mechanism. This involved the formation of an electrochemically generated red solid, consistent with that reported by Forzani *et al.*², where dimerisation of the TNT radical likely forms an azo or azoxy compound. The understanding of the electrochemical reduction mechanism of TNT in RTILs gained in this study will drive toward the development of explosives sensing applications.

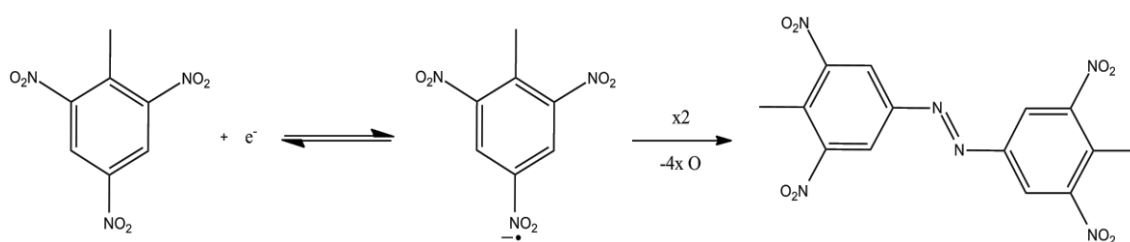


Figure 1: Proposed scheme of the EC₂ mechanism of TNT reduction, forming one of the possible electrogenerated azo products.

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Model Catalysts and Biological Molecules Investigated by Scanning Probe Microscopies

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Scanning Probe Microscopies (SPM) have given the opportunity to investigate surfaces and its adsorbates with unprecedented resolution. This applies in particular to the solid-liquid interface and, specifically, for investigations under in-situ electrochemical conditions. **ElectroChemical Scanning Tunnelling Microscopy (EC-STM)** and more recently **Scanning ElectroChemical Potential Microscopy (SECPM)** can be used to investigate potential dependent phenomena on surfaces, with SECPM being specifically suitable for biological structures.

Two major areas will be discussed: One, where metal particles are deposited on typically Au(111) and carbon surfaces and the reactivity of such particles, e.g. Pd and Pt particles, were investigated regarding the hydrogen reaction. This includes creating single nanoparticles with the tip of an EC-STM whereas the tip was used as a local sensor to determine the reactivity of the single particles [1-3]. Specific reactivity can change by orders of magnitude depending on the density of particles, their size and the kind of substrate.

The second area looks at biological structures, specifically enzyme molecules adsorbed on carbon or Au(111) surfaces. Here EC-STM and SECPM are being employed and their respective capabilities are shown. Charge transfer processes through the enzyme molecule can be studied using EC-STM. Imaging enzyme molecules SECPM shows a higher resolution and a better contrast than EC-STM [4-6].

Both research areas demonstrate the exciting capabilities of SPM under in-situ and also physiological conditions.

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Investigation of the applicability of amorphous $\text{Co}(\text{OH})_2$ on a gold support for electrochemical water splitting and glucose sensing

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Cobalt oxides are promising oxygen evolution catalysts, yet the nature of the active sites and the role of the catalyst structure is still not well understood. Notably, amorphous cobalt oxides, rather than their crystalline counterparts, have recently been reported as efficient oxygen evolution reaction (OER) catalysts in alkaline media [1, 2]. Here we report on the facile and rapid electrochemical formation of amorphous $\text{Co}(\text{OH})_2$ on a gold support for the electrochemical oxidation of water as well as the non-enzymatic electrochemical detection of glucose. We show that amorphous $\text{Co}(\text{OH})_2$ on an underlying gold support demonstrates excellent oxygen evolution capability under alkaline conditions with a current density of 10 mA cm^{-2} at an overpotential of 360 mV, a Tafel slope of 56 mV dec^{-1} and a turnover frequency of 2.1 s^{-1} which maintains its activity for 24 hr of continuous operation. Interestingly, it is also found that there is a synergistic effect between the amorphous $\text{Co}(\text{OH})_2$ and gold towards glucose detection. However, during cyclic voltammetric cycling some conversion to crystalline Co_3O_4 occurs at the very surface of the material but the bulk remains amorphous. This surface crystallization process affects the sensitivity of the response towards both glucose oxidation as well as the OER quite significantly and is discussed in this presentation. This direct and rapid electrochemical approach to the formation of amorphous cobalt hydroxide on a gold support combines the stability advantages and facile preparation method for both the OER and glucose sensing.

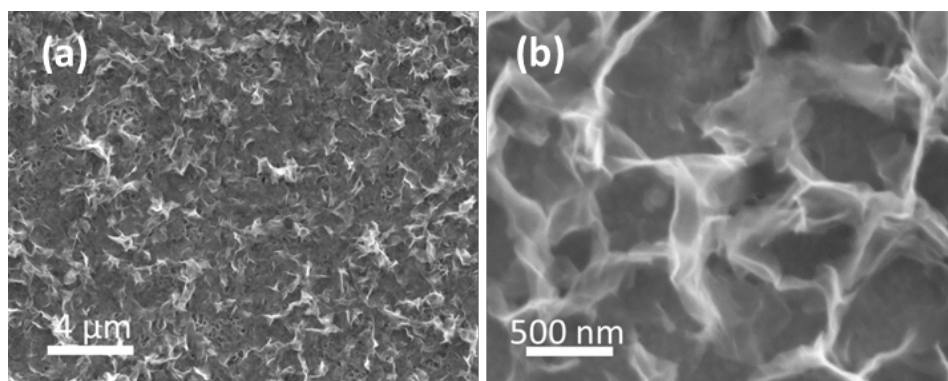


Figure 1. SEM images of electrodeposited $\text{Co}(\text{OH})_2$ on the Au electrode after the CV performed for 10 cycles at 20 mV sec^{-1} .

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Electrochemical Impedance Study of Oxide Films Formed During Electropolishing of Aluminium in Phosphoric Acid

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In electropolishing the surface roughness of a metallic work piece is reduced and its reflectivity increased due to two concurrently active processes: levelling, and brightening i.e. the smoothing of peaks and valleys larger and smaller than 1 μm respectively [1]. Both processes occur simultaneously only if the current is limited by mass transfer, either due to a precipitated salt film or as a result of the limited availability of a solvating or complexing acceptor species in the electrolyte. Combining electrochemical impedance spectroscopy with a rotating disc electrode allows one to distinguish between both mechanisms solely based on the high frequency part of the impedance [2]. In previous studies on the electropolishing of aluminium in perchloric acid/ethanol [3] and AlCl_3 /dimethylsulfone [4] electrolytes a porous salt film and a combination of a compact and a porous salt film were found. It was previously suggested that a compact salt film is also present during the electropolishing of aluminium in hot, concentrated phosphoric acid [5].

In this study, electrochemical impedance spectra were recorded for frequencies ranging from 500 kHz down to 5 Hz in 85% phosphoric acid at 75°C and at different voltages along the limiting current plateau employing a rotating disc electrode made from commercially pure aluminium. The resulting Nyquist plots (figure 1) show three distinct features in the first and second quadrant: a capacitive loop at high and low frequencies and an inductive loop at medium frequencies. Subsequently, the high frequency capacitive loop was fit to an equivalent electrical circuit using a non-linear least squares algorithm. The fitted capacitance values are considerably lower than typical values for a double layer capacitance and range between 1.2 and 3.4 $\mu\text{F}/\text{cm}^2$ indicating the presence of a salt or oxide film along the anode surface in series with the double layer. In accordance with SEM images of electropolished samples, the existence of a porous film can be excluded as the fitted values for the solution resistance vary between 0.61 and 0.68 Ωcm^2 , close to the expected value, and are unaffected both by applied voltage and rotation speed. Assuming a compact film structure instead, the film properties can be calculated based on the high field conduction model [6]. The

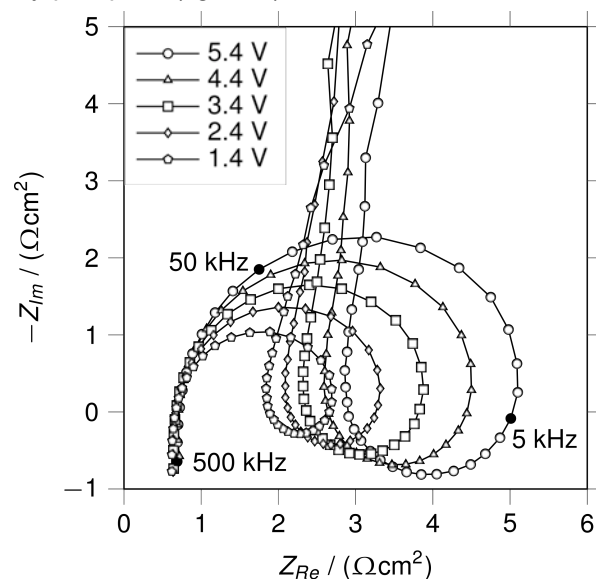


Figure 1: Nyquist plot of impedance data recorded at 75°C, 400 rpm and different applied voltages along the limiting current density plateau.

resulting film thickness lies between 5 and 12 nm and, in general, increases with a rise in applied potential, while rotation speed has little to no effect. Presuming the film consists of Al_2O_3 , the relative permittivity is calculated as 15.4.

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Conductive surfaces responsive to temperature and salt

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Surfaces with readily-modulated properties show great promise in a range of applications, including microfluidic devices, self-cleaning surfaces, and chromatographic substrates. In particular, surface-bound brushes containing poly(ethylene glycol) derivatives have generated a lot of interest due to their biocompatibility, responsiveness to both temperature and salt, and the ability to tailor the conditions under which switching occurs.

We report on the synthesis and characterisation of a novel surface, based on polymer brushes grafted from a conducting poly(3,4-ethylenedioxythiophene) (PEDOT) backbone that has been modified to include ATRP-initiating sites. A range of brushes based on poly(ethylene glycol) methyl ether methacrylate (PEGMMA) were grafted from the PEDOT backbone by AGET ATRP. In solution, these polymers precipitate above a cloud point temperature, which is sensitive to the addition of salts. The cloud point temperature can also be tailored through the brush composition. Characterisation of the surface-bound brushes by ellipsometry and QCM-D (quartz crystal microbalance with dissipation) reveal that they collapse at similar temperatures and salt compositions to the corresponding unbound polymers. In addition, the surfaces are still electroactive after grafting, allowing further characterisation through electrochemical means such as cyclic voltammetry and electrochemical impedance spectroscopy. Coupled with the antifouling nature of the PPEGMMA brushes, these surfaces lend themselves to bioelectronic applications such as biosensing, tissue culture and medical implants.

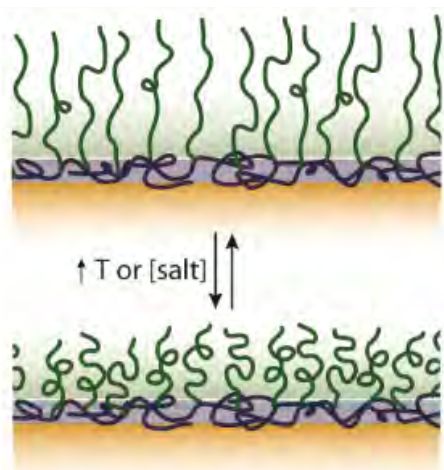


Figure: Salt or temperature-induced collapse of PPEGMMA brushes grafted on PEDOT, leading to a switch in surface properties.

EPR spectroscopic characterisation and fate of a monomeric Pt^{III} species produced via electrochemical oxidation of anticancer compound *trans*-[Pt^{II}{(*p*-BrC₆F₄)NCH₂CH₂NEt₂}Cl(py)]

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Recently we established that highly non-coordinating media provide conditions conducive to formation of monomeric Pt^{III} derivatives in the electrochemical oxidation of the anticancer compound *trans*-[Pt^{II}{(*p*-BrC₆F₄)NCH₂CH₂NEt₂}Cl(py)] under short voltammetric time scales.^[1] Almost quantitative transformation of Pt^{II} to Pt^{III} occurred under short time scale voltammetric conditions. Small concentrations of the paramagnetic monomeric Pt^{III} species remaining after longer timescale bulk electrolysis experiments were identified by EPR spectroscopy. We now report the characterization of some of the products (Pt^{II} organoamineamides) formed by chemical oxidation of the platinum anticancer compound and by exhaustive bulk electrolysis. Relationships between Pt^{III} intermediates and Pt^{II} organoamineamides isolated in this study are considered. Interestingly, some but not all products obtained from chemical oxidation (see Figure 1) are the same as those derived from electrochemical oxidation. Substituted Pt^{II} organoamineamide (A) generated by chemical oxidation gives more stable monomeric Pt^{III} on its electrochemical oxidation and it is stable at longer time scales.

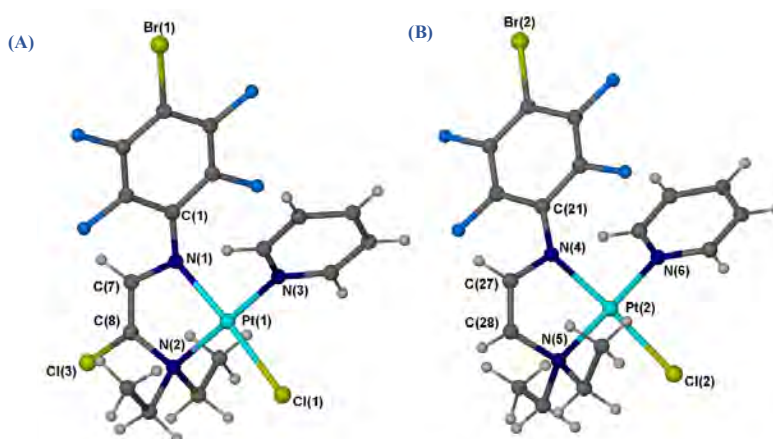


Figure 1. X-ray crystal structures of substituted (A) and non-substituted (B) organoamineamides obtained after chemical oxidation of *trans*-[Pt^{II}{(*p*-BrC₆F₄)NCH₂CH₂NEt₂}Cl(py)] with hydrogen peroxide.

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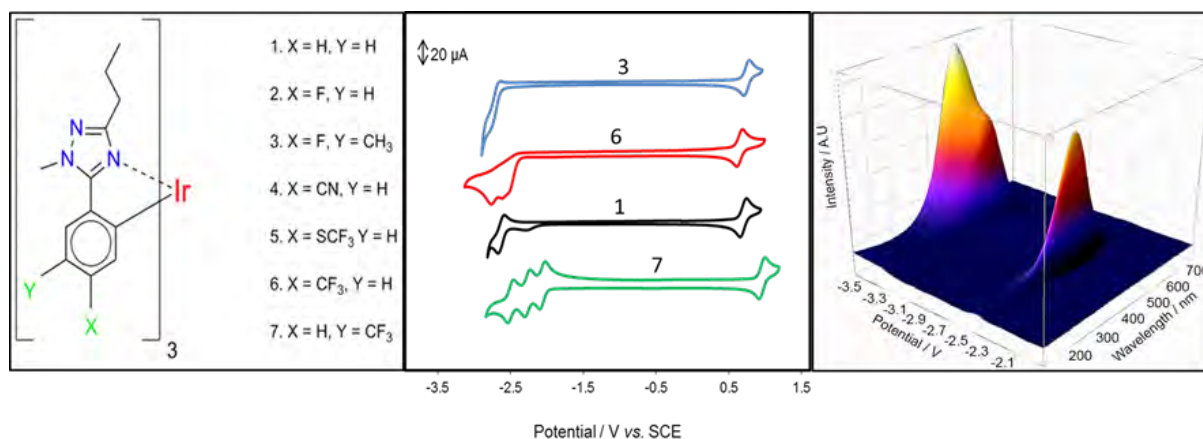
Spectroscopic, electrochemical and electrochemiluminescent properties of highly luminescent iridium(III) 1,2,4-triazole complexes

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The spectroscopy, electrochemistry and electrochemiluminescence (ECL) of a family of blue emitting homoleptic cyclometalated complexes based on *fac*-tris(5-aryl-1,3-disubstituted-[1,2,4]triazolyl)iridium(III) have been investigated. The effect of varying the substituents on the phenyltriazole unit is discussed.



All the complexes are blue-green emitters, showing high photoluminescence efficiencies ($\phi_{\text{PL}} \sim 0.60$ – 0.97) with a single-exponential luminescent lifetime in the range of $(1.81 - 3.49) \mu\text{s}$. A quasi-reversible one-electron oxidation waves in the range of 0.32 to 0.71 V (vs. Fc^+/Fc) in acetonitrile solution which is formally assigned to $\text{Ir(III)} / \text{Ir(IV)}$ redox couple while chemically reversible reductions have not been observed except for the complex with a $(-\text{CN})$ group as a substituent.

Intense blue-green ECL was observed from all the complexes in three modes of ECL generation (annihilation, oxidative-reduction, reductive-oxidation) and ECL efficiencies (ϕ_{ECL}) measured to be in the range of 0.11 to 0.0012 referenced to Ru(bpy)_3^{2+} ($\text{bpy} = 2,2'$ -bipyridine) ($\phi_{\text{ECL}} \sim 0.05$).

An unusual tunable ECL emission observed for the fluorinated complex (3) by varying the reduction potential during the annihilation ECL experiment. The complex ECL emission was ascribed to products generated during the oxidative electrochemical processes and it was found that the emission colour could be varied from red to green to blue by controlling the applied potential. 3D-ECL proved to be a powerful technique to investigate and characterise the complex ECL emission behaviour.

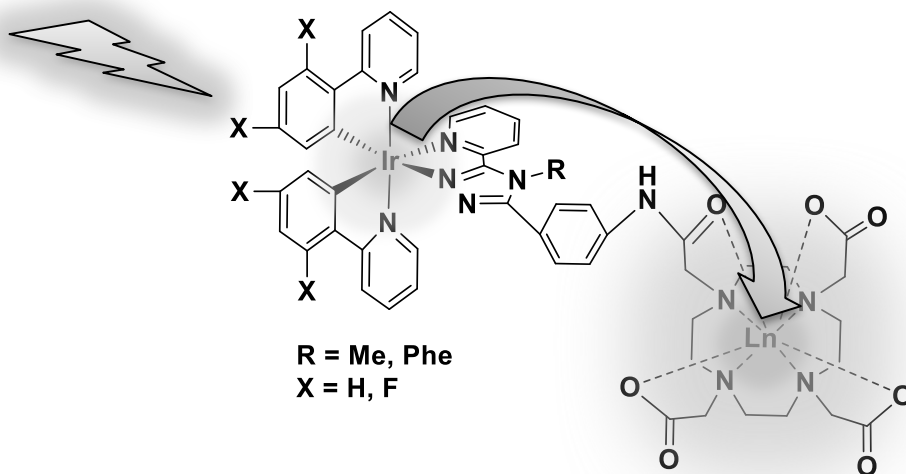
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Electrochemiluminescent energy transfer between d-metal donors and f-block lanthanide acceptors

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Lanthanide's luminescent f-f excited states give very characteristic emission profiles (distinct for each lanthanide ion). The forbidden f-f transitions require sensitizing by "antenna" groups to generate the lanthanide excited state.¹ Electrochemiluminescence (ECL) is a powerful alternative to traditional photoluminescence detection, and lanthanide-based ECL emitters would be highly desirable. However, so far no intense lanthanide-based ECL emitters have been reported.² Electrochemically generated luminescence resonance energy transfer (ECRET) offers a potential mechanism for sensitizing the f-block elements, allowing multiplex sensing arrays.^{3–5} As far as we know, there is no reported emission of f-block lanthanides sensitized by transition metal complexes and initiated by ECL. We have investigated d-f heterobimetallic dyads consisting of Iridium(III) 1,2,4 triazole complex conjugated to the macrocycle 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) which facilitates lanthanide binding. The electrochemical and photophysical properties of this unique structure were investigated. Lanthanide (Ln) titration and isolation experiments were conducted to obtain emission of from Ln acceptor. The mechanism for ECL energy transfer was investigated from these studies.



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POSTERS

Electrochemistry at the glycerol-modified interface between aqueous and organic electrolyte solutions

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) offers a label-free approach to the detection of biomolecules such as proteins. While protein adsorption/desorption at these interfaces can be utilized for detection of low concentrations, there is little information about the structural changes that proteins undergo in these processes, which encompass applied electric fields, adsorption/desorption, and complexation with electrolyte ions. In this work, voltammetry at an array of micro-ITIES was undertaken in which the aqueous phase was modified by the presence of glycerol. Such a system provides a basis for future bulk phase spectrophotometric analysis of proteins at the interface using methods that are protein structure-sensitive. The present work is concerned with establishing the electrochemical behavior of the glycerol-modified micro-ITIES array.

Initially, matrix effects associated with increasing glycerol concentrations in the aqueous phase were characterised using cyclic voltammetry and well-defined simple ion transfer processes. It was found that the potential window, defined by the transfer of background electrolytes from either phase to the adjoining phase, was significantly reduced for high glycerol proportions. Similarly, shifts in the transfer potential of the tetraethylammonium ion (the model analyte species used to probe the interface behavior) were observed. Steady-state currents, characteristic of radial diffusion of the analyte towards the micro-interfaces, were observed and were seen to decrease linearly with inverse viscosity of the glycerol-aqueous phase. This indicated that increased solution viscosity and subsequent reduction in diffusion coefficient was the primary factor in reducing the magnitude of the current response. Finally, lysozyme from hen egg white (HEWL) was used as a model protein analyte to investigate the possibility of characterising protein interfacial interactions under the required conditions. HEWL was detected by voltammetry at glycerol compositions of up to 80 %(vol). The results presented indicate that glycerol modifies the behavior of the ITIES but that ion-transfer processes can be implemented and studied and, as a result, open up the opportunity for studies by spectrophotometric methods.

Investigation of Fucoidan Extracts at the Interface Between Two Immiscible Electrolyte Solutions

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Having an array of biological activities like retrovirus inhibition [1] and cancer treatment [2], Fucoidans have been and continue to be the center of numerous researches with the common aim of developing a direct method for its detection even in complex sample matrices. This class of sulphated polysaccharides are extracted mostly from seaweeds as well as other marine invertebrates and is mostly formed with an $\alpha(1-3)$, or alternating $\alpha(1-3)$ and $\alpha(1-4)$ connected L-fucose segments. Various branch points like acetyl groups and sulphates appear periodically in its polymer chain [3].

Electrochemical investigation at the interface between two immiscible electrolyte solutions (ITIES) is a rising analytical technique that is used to study biomolecules and is known to offer the advantage of label-free detection even for non-redox active target analytes [4]. This method was utilized to study the electrochemical characteristics of Fucoidan polyelectrolytes. Voltammetry and adsorption techniques were employed to study the Fucoidan extracts under different conditions: varying the aqueous phase pH, scan rate, adsorption potential and adsorption times.

Results showed that the more promising response was achieved at aqueous phase pH 12, when the polyelectrolytes were mostly deprotonated. The varying structure between species studied (*Undaria pinnatifida* and *Fucus vesiculosus*) had an impact on the behavior of these extracts at the polarized water-organogel interface and this is in agreement with previous studies employing polyion-sensitive membrane electrodes [5]. *Undaria* showed a more intense current response compared to *Fucus* around 0.15-0.25 V, which can be attributed to the presence of more galactose units in its polymer backbone. Consequently, a lower detectable concentration was observed for *Undaria* at 50 $\mu\text{g/mL}$ while *Fucus* was detectable at 300 $\mu\text{g/mL}$ using cyclic voltammetry. However, application of a pre-concentration step promises lower detection, with 20 $\mu\text{g/mL}$ for *Undaria* after only 60 s.

The latest results on Fucoidan extract characterization and detection at the ITIES will be presented and discussed.

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Electrogenerated Chemiluminescence of Tris(2,2' bipyridine)ruthenium(II) Using Common Biological Buffers As Co-reactant, pH Buffer and Supporting Electrolyte

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Electrogenerated chemiluminescence (also known as electrochemiluminescence or ECL) is the emission of light from an electrochemically initiated reaction. Current commercial ECL systems use tripropylamine (TPA) as the co-reactant, but this compound is toxic, volatile and it is usually required in relatively high concentrations to attain good sensitivity (100 mM). New co-reactants such as the far less toxic 2-(dibutylamino)ethanol (DBAE) have been proposed as an alternative safer co reactant, but its response is somewhat sensitive to electrode material and other experimental conditions. In this project a series of common pH buffers that contain tertiary amines (POPSO sesquisodium salt, EPPS, HEPES Sodium Salt and BIS TRIS hydrochloride salt), often referred to as 'biological buffers', were examined as alternative, non-toxic co-reactants for tris(2,2'-bipyridyl)ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}$) ECL. These biological buffers produce ECL intensities lower than those observed when TPA is used as the co-reactant under similar experimental conditions. However, the fact that these buffers can fulfil the roles of the co-reactant, pH buffer and electrolyte simultaneously, whilst still achieving very good (nanomolar) levels of detection of $[\text{Ru}(\text{bpy})_3]^{2+}$, greatly simplifies the analytical procedure.

Gelification of an ionic liquid with a polymer to improve the robustness of electrochemical gas sensors

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In recent years, room temperature ionic liquids (RTILs) have been investigated as a replacement for traditional electrolytes in sensors due to their many favourable properties including wide electrochemical windows, intrinsic conductivity, high chemical and physical stability and the ability to dissolve a wide range of analyte gases.¹⁻³ In particular, the non-volatile nature of RTILs eliminates the need for a membrane, and they have been suggested as electrolytes in “membrane-free” gas sensors.³ However, one of the issues with “membrane-free” sensors is that they are not very robust for portable applications due to electrolyte leakage e.g. if the sensor is turned on its side.

In this work 2, the electrochemical reduction of oxygen (O₂) has been studied on a new type of commercially-available integrated Pt thin-film electrode (TFE) (Fig. 1). Chemically reversible (but electrochemically quasi-reversible) cyclic voltammetry was observed in the room temperature ionic liquid (RTIL) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₂mim][NTf₂]), showing superior behaviour of TFEs compared to screen-printed electrodes for oxygen sensing. As a step towards the preparation of robust gas sensors, the RTIL was then mechanically stabilised on the TFE surface by mixing with poly(methyl methacrylate) (PMMA) to form a gel-polymer electrolyte (GPE). Experiments were conducted at increasing concentrations of PMMA in the PMMA-RTIL mixture, from 0 to 50 % mPMMA/mTot. The peak currents systematically decreased with increasing PMMA content, but all mixtures showed diffusion-controlled voltammetry for oxygen reduction. All the mixtures gave chemically reversible voltammetry, but there was an increase in peak-to-peak separations, especially at high PMMA concentrations, suggesting that the iR (Ohmic) drop is greater in the more viscous media. Linear calibration curves were observed for 10-100 % vol. oxygen at all PMMA-RTIL mixtures studied. The sensitivity was found to decrease as [PMMA] increases, but there was no systematic effect on the LOD.

Lastly, the robustness of the TFE/GPE device has been evaluated by placing the sensor in various geometries (see Fig. 2). It is shown that by employing an adequate amount of PMMA to form a physical gel, a robust, spill-less oxygen gas sensor can be easily achieved. These results demonstrate that the addition of PMMA can improve the mechanical stability of the RTIL film, and hence the robustness of sensors incorporating them, whilst having minimal impact on the LOD and a predictable impact on sensitivity. The PMMA-RTIL mixture was also found to be less impacted by the presence of ambient moisture, which could lead to potentially more robust “membrane-less” and “spill-less” sensors for real world gas sensing applications.

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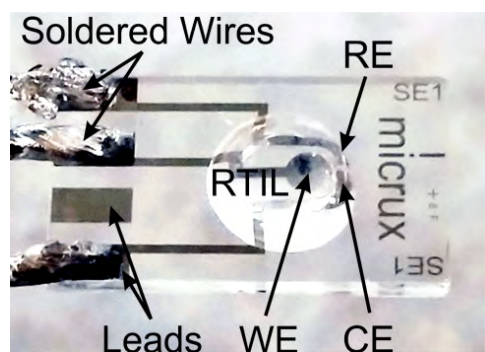


Fig. 1 Photo of a Pt-TFE (purchased from Micrux) with a layer of GPE deposited over the electrodes.

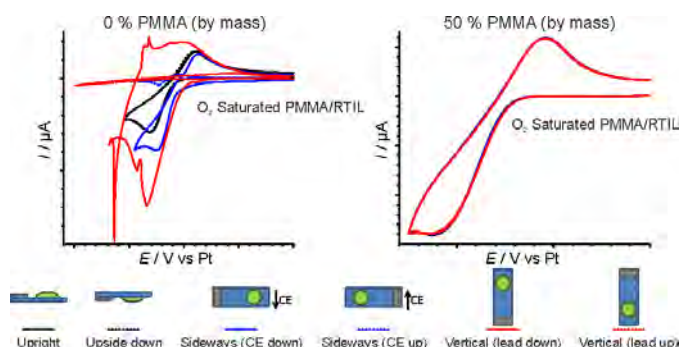


Fig. 2 CVs of O₂/O₂^{•-} redox couple in the neat [C₂mim][NTf₂] and the 50% PMMA doped [C₂mim][NTf₂], with the Pt-TFE positioned in different orientations.

Low Cost Sensing of Pseudoephedrine with Electrochemiluminescence Detection Using Mobile Phone

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Pseudoephedrine (PSE) is sympathomimetic amine with central nervous system stimulating properties. The International Olympic Committee has put the ephedrine on their list of prohibited doping substance and have adopted urinary threshold concentrations, above which an athlete is regarded as positive [1]. Moreover there is a need to assess the presence and concentration of PSE at clandestine drug laboratory crime scenes. In this work, detection of (PSE) as a coreactant using ECL in aqueous solution with $\text{Ru}(\text{bpy})_3^{2+}$ is described. Cyclic voltammetry (CV) and ECL experiments were carried out to determine if the electrochemistry and maximum light of the luminophore in presence of coreactant were affected in any way by changing the electrode material from carbon to ITO or using the 2-electrode set up instead of 3-electrode set up. PSE could be detected to the level of $2.45 \mu\text{M}$ and $17.82 \mu\text{M}$ using glassy carbon and ITO electrode respectively with the high voltage power supply. In the next step Paper-based microfluidic sensors based on ECL detection are fabricated simply and cheaply. The paper fluidic element was then placed in face-to-face contact with 2 ITO electrodes and both were tightly enclosed in clear plastic using a common office laminator. A mobile camera phone can also be used to detect the luminescence from the sensors by analyzing the red pixel intensity in digital images of the ECL emission [2].

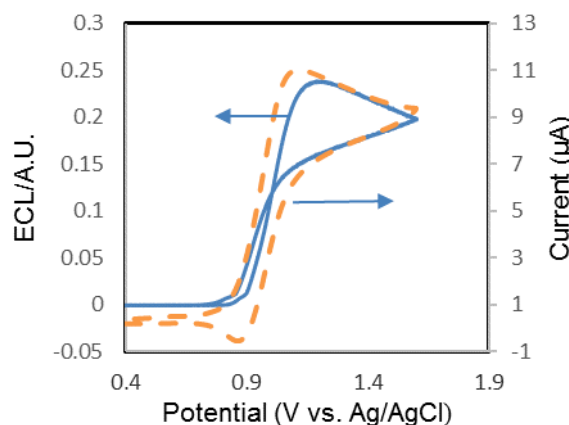


Fig 1. Response for $1\text{mM Ru}(\text{bpy})_3^{2+}$ solution in presence of PSE 1mM in pH 10 phosphate buffer.

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