Program of the

19th Topical Meeting of the International Society of Electrochemistry

Electrochemistry at Modified Interfaces

17- 20 April 2016
Auckland, New Zealand

Organized by:
Division 1 Analytical Electrochemistry
Division 4 Electrochemical Materials Science
ISE Region Australia-New Zealand

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Organizing Committee

Fethi Bedioui, *ParisTech/CNRS, France*
Nick Birbilis, *Monash University, Australia*
Alison Downard, *University of Canterbury, New Zealand* (Co-Chair)
Conor Hogan, *La Trobe University, Australia*
Mary Ryan, *Imperial College London, UK*
David Williams, *University of Auckland, New Zealand* (Co-Chair)

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Sunday 17 April 2016

Welcome Reception

17:30 to 19:00

THE UNIVERSITY
OF AUCKLAND
NEW ZEALAND

Neon Foyer, Faculty of Engineering, 20 Symonds St, Auckland

Monday 18 April 2016 - Morning

08:45 to 09:00 **Opening Ceremony in Theatre 1.439**

Chaired by: Alison Downard and David Williams

Keynote

Theatre 1.439

Chaired by: Alison Downard

09:00 to 09:40 Keynote

Justin Gooding *(School of Chemistry, The University of New South Wales, Sydney, Australia)*, Moinul Choudhury, Simone Ciampi, Vinicius Goncales, Stephen Parker, Roya Tavallaie, Ying Yang, Leila Zarei

Light activated electrochemistry: A strategy for performing voltammetry on a monolithic surface where you want, when you want with micron scale spatial resolution

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Session 1

Room 3.402

Chaired by: Fethi Bedioui

09:50 to 10:10

Conor Hogan *(Chemistry & Physics, La Trobe University, Melbourne, Australia)*, Kiran Bano, Darrell Elton, Seng Loke

Introducing Android Voltammetry

10:10 to 10:30

Dodzi Zigah *(Institute of Molecular Sciences, University of Bordeaux, Talence, France)*

Bipolar Electrochemistry in Materials Science

10:30 to 10:50

Jiri Barek *(Department of Analytical Chemistry, Charles University in Prague, Faculty of Science, Prague 2, Czech Republic)*, Ales Danhel, Jan Fischer, Miroslav Fojta, Andrea Hajkova, Vlastimil Vyskocil

Modified Electrodes Based on Non-Traditional Electrode Materials

10:50 to 11:20 Coffee Break

11:20 to 11:50 Invited

Hubert Girault *(Laboratoire d'Electrochimie Physique et Analytique, Switzerland)*, J. Hidalgo, A. Olaya, P. Peljo, L. Rivier, E. Smirnov

Modified & functional liquid-liquid interfaces

11:50 to 12:10

Eva Alvarez de Eulate *(Chemistry Department, Curtin University, Perth, Australia)*, Damien Arrigan, Yang Liu, Kane O'Donnell, Jorg Strutwolf

Laser-Ablated Micropore Glass Membranes to Modulate Soft Electrochemical Interfaces

12:10 to 12:30

Damien Arrigan *(Chemistry, Nanochemistry Research Institute, Curtin University, Perth, Australia)*, Chris Aldrich, Mark Buntine, Thomas Cornwell, Yang Liu, Anthony O'Mullane, Rhys Tilbury

Glucose oxidation at stochastic nanoparticle electrodes: gold nanoparticles produced by laser ablation

12:30 to 12:50

Micheal D. Scanlon *(Department of Chemistry, University College Cork, Cork, Ireland)*, Andres Felipe Molina Osorio

Electro-adsorption of Porphyrin Films at Polarised Soft Interfaces

Session 2

Theatre 1.401

Chaired by: Viola Birss

09:50 to 10:10

Gabriel Loget *(Institut des Sciences Chimiques de Rennes, CNRS - Université de Rennes 1, Rennes, France)*, Patrik Schmuki

Modification of Ti Surfaces with Gradients of TiO_2 Nanotubes by Bipolar Anodization

10:10 to 10:30

Iwona Rutkowska *(Department of Chemistry, University of Warsaw, Warsaw, Poland)*, Pawel J. Kulesza, Anna Wadas

Generation of nanoreactors at electrocatalytic interfaces: controlled distribution of distinct noble metal sites within nanostructured mixed-metal oxide supports

10:30 to 10:50

Hoe Chul Kim *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Seunghoe Choe, Myung Jun Kim, Young Gyu Kim, Jae Jeong Kim, Yoonjae Lee, Youngran Seo

Bottom-up Filling of Through Silicon Vias Based on Electrochemically Derived Filling Mechanism with Ammonium-Containing levelers

10:50 to 11:20

Coffee Break

11:20 to 11:50 Invited

Anthony O'Mullane *(School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, Australia)*, Tenille Herd, Md Abu Sayeed

Electrochemical Deposition of Mixed Metal Systems and Their Electrocatalytic Properties

11:50 to 12:10

Andrzej Czerwinski *(Faculty of Chemistry, University of Warsaw, Warsaw, Poland)*, Katarzyna Hubkowska, Urszula Koss, Mariusz Lukaszewski, Zbigniew Rogulski

The influence of composition Pd alloys on hydrogen electrosorption

12:10 to 12:30

Bing-Joe Hwang *(Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan)*

Nanocatalysts for Hydrogen Evolution Reaction

12:30 to 12:50

Daniel Scherson *(Chemistry, Case Western Reserve University, Cleveland, USA)*, Nicholas Georgescu, Adriel Jebaraj

Bromide Adsorption Effects on the Electrocatalytic Reduction of Hydrogen Peroxide on Pt in Acid Solutions

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Session 3

Room 3.404

Chaired by: Dan Buttry

09:50 to 10:10

Sung Mook Choi *(Surface Technology Division, Korea Institute of Materials Science (KIMS), Changwon, Korea)*

Electrocatalytic properties of 0, 1 D metal oxide catalysts for oxygen evolution reaction in alkaline media

10:10 to 10:30

Ali Hosseini *(Department of Chemical and Materials Engineering, The University of Auckland, Auckland, New Zealand)*

Proton Switch for Modulating Oxygen Reduction by a Copper Electrocatalyst Embedded in a Hybrid Bilayer Membrane

10:30 to 10:50

Justyna Piwowar *(Department of Chemistry, University of Warsaw, Warsaw, Poland)*, Adam Lewera

Activity and Selectivity of Unsupported Pt, Rh and Pt-Rh Nanocatalysts towards Oxidation of Ethanol to CO_2, Acetic Acid and Acetaldehyde

10:50 to 11:20 Coffee Break

11:20 to 11:50 Invited

Anthony Kucernak *(Chemistry, Imperial College London, London, United Kingdom)*, Biraj Kakati

Corrosion is not always bad – using corrosion-like processes to remove poisons on electrocatalysts

11:50 to 12:10

Mitsuharu Chisaka *(Graduate School of Science and Technology, Hirosaki University, Hirosaki, Japan)*, Yuta Ando, Noriaki Itagaki, Yusuke Yamamoto

Is Catalyst-Support Interface Necessary for Oxygen Reduction Reaction on TiN-Core Covered with Nitrogen-Doped Rutile-Shell Catalysts?

12:10 to 12:30

Alexander Oleinick *(Departement de Chimie, CNRS - Ecole Normale Superieure, Paris, France)*, Christian Amatore, Michael Mirkin, Irina Svir, Yun Yu, Min Zhou

Nanoelectrochemical Detection of Short-Lived Intermediates of Electrocatalytic Oxygen Reduction: Elucidation of the Reaction Mechanism

12:30 to 12:50

Ichizo Yagi *(Faculty of Environmental Earth Science, Hokkaido University, Sapporo, Japan)*, Masaru Kato, Nobuhisa Oyaizu, Katsuaki Shimazu

Oxygen reduction reaction at self-assembled monolayers of copper-based electrocatalysts on a polycrystalline Au electrode

Monday 18 April 2016 - Afternoon

Keynote

Theatre 1.439

Chaired by: David Williams

13:50 to 14:30 Keynote

Ulrich Stimming *(School of Chemistry, Newcastle University, Newcastle upon Tyne, United Kingdom)*, Jochen Friedl

Vanadium Electron Transfer on Modified Carbon Electrodes

Session 1

Room 3.402

Chaired by: Damien Arrigan

14:40 to 15:00

Li-Jun Wan *(Institute of Chemistry, Chinese Academy of Sciences, Beijing, and University of Science and Technology of China, Hefei, China)*

Surface Molecular Engineering for Electrode Modification: Preparation and Characterization by *in-situ* STM

15:00 to 15:20

Shuehlin Yau *(Chemistry, National Central University, Jhongli, Taiwan)*

Effects of Benzenediols on the Oxidative Polymerization of Aniline on Au(111) – Electrochemistry and Scanning Tunneling Microscopy

15:20 to 15:40

Cherie Tollemache *(School of Chemical Sciences, University of Auckland, Auckland, New Zealand)*, Penelope J. Brothers, Ali Hosseini, Ashton Partridge

In Situ Deprotection and Self Assembly of Mixed Monolayers from Thioacetyl-Containing Alkanethiols on Gold Surfaces

15:40 to 16:10 Coffee Break

16:10 to 16:30

Corinne Lagrost *(Institut des Sciences Chimiques de Rennes, CNRS and University of Rennes 1, Rennes, France*), Jean-François Bergamini, Janine Carvalho Padilha, Jean-Marc Noël, Joëlle Rault-Berthelot

Reductive Grafting of *In Situ* Produced Diazonium Cations in a Brønstedt Acidic Ionic Liquid – Evidence of an Efficient Self-Limiting and Self-Patching Film Growth

16:30 to 16:50

Yann Leroux *(Institut des Sciences Chimiques de Rennes, CNRS, University of Rennes 1, Rennes, France)*, Didier Astruc, Roberto Ciganda, Philippe Hapiot, Joanna Jalkh, Sébastien Lhenry, Catia Ornelas, Jaime Ruiz

Electrochemical Response of Redox Dendrimers as surface modifiers and redox probes in SECM experiments

16:50 to 17:10

Alison Downard *(Department of Chemistry, University of Canterbury, Christchurch, New Zealand)*, Tony Breton, Eric Levillain, Thibaud Menanteau

Tuning of the Diazonium Electrografting using Radical Scavenger

Session 2

Theatre 1.401

Chaired by: Alan Bond

14:40 to 15:00

Tania Benedetti *(IPRI/ACES, University of Wollongong, Wollongong, Australia)*, Sima Aminorroaya-Yamini, Rouhollah Jalili, David Officer, Gordon Wallace

Exfoliated MoS_2 and ionic liquids for catalysis of CO_2 electro-reduction

15:00 to 15:20

Daniel Buttry (*School of Molecular Sciences, Arizona State University, Tempe, USA)*

Electrochemical Capture and Release of Carbon Dioxide Using A Thiolate/Disulfide Redox Couple in Ionic Liquid Media

15:20 to 15:40

Aaron Marshall *(Department of Chemical and Process Engineering, Univ. of Canterbury, Christchurch, New Zealand)*, David Harrington, Calvin Lim

TiO_2 modified Cu cathodes for electrocatalytic CO_2 reduction

15:40 to 16:10 Coffee Break

16:10 to 16:30

Damian Kowalski *(Faculty of Chemistry, University of Warsaw, Warsaw, Poland)*

Synthesis and Modification of Anodic TiO_2 Nanotubes

16:30 to 16:50

Pawel J. Kulesza *(Department of Chemistry, University of Warsaw, Warsaw, Poland)*

Functionalization of electrochemical interfaces toward efficient solar energy conversion and catalytic reduction of carbon dioxide

16:50 to 17:10

Hanna Sopha *(Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic)*, Marketa Jarosova, Petr Knotek, Jan M. Macak

Towards Improved Ordering of Self-Organized TiO_2 Nanotube Layers

Session 3

Room 3.404

Chaired by: Daniel Scherson

14:40 to 15:00

Jun Chen *(Australian Institute of Innovative Materials, University of Wollongong, Wollongong, Australia)*, Yuyang Hou

CNTs/Graphene Aerogel as Cathode Materials for Lithium-Oxygen Batteries

15:00 to 15:20

Yu-Ting Weng *(Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan)*

Novel Surface Modification of Graphite with Excellent Performance for Lithium-ion Battery

15:20 to 15:40

Nae-Lih Nick Wu *(Chemical Engineering Department, National Taiwan University, Taipei, Taiwan)*

Enhanced Performance of Li-Ion Battery Graphite Anode by Polymeric Artificial Solid-Electrolyte-Interphase and Its Underlying Mechanism

15:40 to 16:10 Coffee Break

16:10 to 16:30

Farshad Barzegar *(Physics, University of Pretoria, Pretoria, South Africa)*

Preparation and characterization of three-dimensional nanoporous carbon from expanded graphite for high energy density supercapacitor in aqueous electrolyte

16:30 to 16:50

Bernhard Gollas *(Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria)*, David Fuchs, Robert Schennach, Luciana Vieira

The Carbon Electrode/Deep Eutectic Solvent Interface - Electrochemistry and Spectroelectrochemisry

16:50 to 17:10

Ramesh T. Subramaniam *(Physics, Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia)*, Chiam Wen Liew

Poly(acrylic acid)–based Hybrid Inorganic–Organic Electrolytes for Electrical Double Layer Capacitors Application

Tuesday 19 April 2016 - Morning

Keynote

Theatre 1.439

Chaired by: David E. Williams

09:00 to 09:40 Keynote

Mary P. Ryan *(Department of Materials and London Centre for Nanotechnology, Imperial College, London, United Kingdom)*, Shu Chen, Angela E. Goode, Mohamed Koronfel, Bey Fen Leo, Basma Othman, Alexandra E. Porter, Theresa Tetley, Ioannis Theodorou, Andrew Thorley

Understanding the Bioreactivity of Nanoparticles: Toxicity and Therapeutics

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Session 1

Room 3.402

Chaired by: Philippe Hapiot

09:50 to 10:10

Fethi Bedioui *(Technologies Chimiques et Biologiques pour la Sante, Chimie ParisTech/CNRS/INSERM/Paris Descartes, Paris, France)*, Victor Baldim, Marcelo de Oliveira, Sophie Griveau, Abdulghani Ismail, Patricia Taladriz Blanco

Amperometric Quantification of Plasma S-nitrosothiols Using Gold Nanoparticles

10:10 to 10:30

Wenrong Yang (*School of Life and Environmental Sciences, Deakin University, Waurn Ponds, Australia)*

Ultrasensitive Detection of Chiral Molecules by Tunneling Current through Gold Nanoparticle Networks

10:30 to 10:50

Emelyne Gervais *(Laboratoire de Génie Chimique, Université Paul Sabatier, Toulouse, France)*, David Evrard, Pierre Gros

Hg(II) ultra-fast trace determination using square-wave anodic stripping voltammetry on a glassy carbon electrode functionalized by a mixed diazonium/gold nanoparticles layer

10:50 to 11:20

Coffee Break

11:20 to 11:50 Invited

Richard McCreery *(Department of Chemistry, University of Alberta, Edmonton, Canada)*, Akhtar Bayat, Adam Bergren, Oleksii Ivanshenko, Amin Morteza

Molecular Rectification and Electron Transport in "Highly" Modified Electrodes

11:50 to 12:10

Alexander Rudnev *(Department of Chemistry and Biochemistry, University of Bern, Bern, Switzerland)*, Andrea Droghetti, Masa-aki Haga, Veerabhadrarao Kaliginedi, Akiyoshi Kuzume, Hiroaki Ozawa, Ivan Rungger

Effect of Anchoring Chemistry on Charge Transport through Au/Molecule/HOPG Junctions

12:10 to 12:30

Sze-yin Tan *(School of Chemistry, Monash University, Clayton, Australia),* Alan Bond, Julie V. Macpherson, Patrick R. Unwin, Jie Zhang

Impact of Adsorption on Scanning Electrochemical Microscopy (SECM) Measurements and Implications for Nanoscale Geometries

12:30 to 12:50

Thomas Doneux *(Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles (ULB), Brussels, Belgium)*, Nicolas Brouette, Claudine Buess-Herman, Alexis de Ghellinck, Michele Sferrazza, Eleonore Triffaux

Electron Transfer Across an Antifouling Mercapto-hepta(ethylene glycol) Self-Assembled Monolayer

Session 2

Theatre 1.401

Chaired by: Mary Ryan

09:50 to 10:10

Mario Ferreira *(Department of Materials and Ceramic Engineering, University of Aveiro, Aveiro, Portugal)*, Dzmitry Ivanou, Andrei Salak, Maksim Starykevich, Mikhail Zheludkevich

Effect of Alumina and Titania Barrier Layer on Zinc Electrodeposition from Deep Eutectic Solvent

10:10 to 10:30

David Williams (School of Chemical Sciences, University of Auckland, Auckland, New Zealand) Jane Leung, Yiwen Pei, Jadranka Travas-Sejdic, David Williams

Switchable Surfaces of Electrochemically-Active Conducting Polymers

10:30 to 10:50

Maksim Starykevich *(Department of Materials Engineering and Ceramic, University of Aveiro, Aveiro, Portugal)*, Mario Ferreira, Dzmitry Ivanou, Andrei Salak, Mikhail Zheludkevich

Electrodeposition of zinc 1-D nanoparticles in porous titania template from deep eutectic solvent

10:50 to 11:20

Coffee Break

11:20 to 11:50 Invited

Nick Birbilis *(Materials Science and Engineering, Monash University, Clayton, Australia)*, Sebastian Thomas

Aqueous electrochemistry of magnesium

11:50 to 12:10

Bridget Ingham *(Advanced Materials, Callaghan Innovation, Lower Hutt, New Zealand)*

In situ Synchrotron X-ray Studies of Interfaces Under Electrochemical Control

12:10 to 12:30

Wejdene Mastouri *(Department of Physics and Mechanics of Materials, Institut Pprime, Poitiers, France*), Serguei Martemianov, Luc Pichon, Anthony Thomas

Study of the electrical double layer at the solid (304L) / liquid (NaCl solution) interface

12:30 to 12:50

Sachiko Ono *(Department of Applied Chemistry, Tokyo, Japan)*, Hidetaka Asoh, Akihiko Koshi, Jinsun Liao, Yoichi Mori, Shuichi Moronuki

Effect of Electrolyte Concentration on Structure and Corrosion Resistance of Anodic Films Formed on Magnesium by Plasma Electrolytic Oxidation

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Session 3

Room 3.404

Chaired by: Hubert Girault

09:50 to 10:10

Diego Fernando Quintero Pulido *(Department of EEMCS, Twente University, Enschede, Netherlands)*, Johann Hurink, Gerard Smit, Marnix Ten Kortenaar, Miheer Vaidya

Electrochemical Oxidation of Glycerol and Reduction of Oxygen in Alkaline Media

10:10 to 10:30

Arnaud Serres *(PPME, Universite de la Nouvelle-Caledonie, Noumea, New Caledonia)*, Charlotte Carré, Peggy Gunkel-Grillon, Marc Jeannin, Rene Sabot

The use of a bi-metallic structure under cathodic protection in seawater favors a 3D calcareous growth imitating the coral structure

10:30 to 10:50

Luis F. Arenas *(Faculty of Engineering and the Environment, University of Southampton, Southampton, United Kingdom)*, Carlos Ponce de León, Frank C. Walsh

Electrode Performance in Industrial Processes Involving Cerium Conversion

10:50 to 11:20 Coffee Break

11:20 to 11:50 Invited

Byungchan Han *(Department of Chemical & Biomolecular Engineering, Yonsei University, Seoul, Korea)*

Design of Active and Durable Catalysts with Non-precious Materials for Oxygen Reduction and Evolution Reactions: First Principles Prediction and Experimental Validation

11:50 to 12:10

Rafal Jurczakowski *(Faculty of Chemistry, University of Warsaw, Warsaw, Poland)*, Pawel Kulboka, Piotr Polczynski

High Frequency Impedance Spectroscopy of Hydrogen Electrosorption in Thin Palladium Films Covered by Platinum Monolayers

12:10 to 12:30

Benchaporn Lertanantawong *(Pilot Plant Development and Training Institute, King Mongkut's University of Technology Thonburi, Bangkok, Thailand)*, Anthony Peter O'Mullane, Werasak Surareungchai

Influence of Nanoparticle-Electrode Collisions on the Electrodeposition of Pt Nanostructures and their Electrocatalytic Properties

Tuesday 19 April 2016 - Afternoon

Session 1

Room 3.402

Chaired by: Frédéric Barrière

13:50 to 14:20 Invited

Neso Sojic *(ISM - ENSCBP, University of Bordeaux, Pessac, France)*, Haidong Li, Florent Pinaud, Valérie Ravaine

Antagonist Effects Leading to Enhanced Electrogenerated Chemiluminescence in Thermoresponsive Hydrogel Nanomaterials

14:20 to 14:40

David Evrard *(Laboratoire de Génie Chimique, University Paul Sabatier, Toulouse, France)*, Loïc Assaud, Brigitte Caussat, Véronique Conédéra, Pierre Gros, Nicolas Massonnet, Marc Monthioux, Laure Noé, Ludovic Salvagnac, Pierre Temple-Boyer, Hugues Vergnes

Mixed diazonium/PEDOT-functionalized graphene electrode for antioxidant biomarkers detection: proof-of-concept for integration on silicon substrate

14:40 to 15:00

Vinicius Goncales *(School of Chemistry, The University of New South Wales, Sydney, Australia)*, Simone Ciampi, Justin Gooding, Bakul Gupta, Stephen Parker, Yangfang Wu, Ying Yang

The importance of the Hofmeister series on the ability of ions and water to penetrate through self-assembled monolayers; Implications for device fabrication on Si(100) surfaces

15:00 to 15:20

Valentina Pifferi *(Dipartimento di Chimica, Università degli Studi di Milano, Milan, Italy)*, Silvia Ardizzone, Giuseppe Cappelletti, Luigi Falciola, Daniela Meroni, Guido Panzarasa, Guido Soliveri

Photo-renewable engineered sensor based on silica, silver nanoparticles and titania

15:20 to 15:50 Coffee Break

15:50 to 16:10

Debbie Silvester *(Nanochemistry Research Institute, Department of Chemistry, Curtin University, Perth, Australia)*, Ghulam Hussain, Junqiao Lee, Krishnan Murugappan

Gas Sensing in Ionic Liquids on Miniaturised Electrodes: Screen-Printed Electrodes, Thin-Film Electrodes and Thin Ionic Liquid Layers

16:10 to 16:30

Junqiao Lee *(Department of Chemistry, Curtin University, Salter Point, Australia)*, Damien Arrigan, Gert Du Plessis, Debbie S. Silvester

Polymer Gelification of an Ionic Liquid for Electrochemical Gas Sensing

16:30 to 16:50

Leigh Aldous *(School of Chemistry, UNSW Australia, Sydney, Australia)*, Hamoud Alnazzal, Benjamin Lau

Heavy Metal Quantification at Bismuth Electrodes in Biomass-Dissolving Electrolytes – Significant Cation Effect Upon the Interface

16:50 to 17:10

Luigi Falciola *(Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy)*, Valentina Pifferi

Electroanalytical Performances of Electrodes Modified with Porous Layers of Carbon Nanotubes or Ion-Exchange Polymers

Session 2

Theatre 1.401

Chaired by: Ulrich Stimming

13:50 to 14:20 Invited

Viola Birss *(Chemistry, University of Calgary, Calgary, Canada)*, Dustin Banham, Felicia Feng, Farisa Forouzandeh, Abraham Joseph, Xiaoan Li, Siyu Ye

Effect of Surface Modification of Carbons on Their Electrochemical Properties in PEM Fuel Cell Applications

14:20 to 14:40

Prabeer Barpanda *(Materials Research Center, Indian Institute of Science, Bangalore, India)*

Halidated Carbons for Hybrid Electrochemical Supercapacitors: Interface Analysis for Faradaic Activity

14:40 to 15:00

Daniel Bélanger *(Chimie, Université du Québec à Montréal, Montréal, Canada)*, Diby Benjamin Ossonon

Electrochemical exfoliation and functionalization of graphene sheets

15:00 to 15:20

Roberto Torresi *(Instituto de Química, Universidade de São Paulo, São Paulo, Brazil)*, Peter J. Hall, Vitor L. Martins, Anthony J. R. Rennie, Nedher Sanchez-Ramirez

Ionic Liquids as Electrolytes for Electrochemical Double Layer Capacitors

15:20 to 15:50

Coffee Break

15:50 to 16:10

Md Abu Sayeed *(Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, Australia)*, Anthony Mullane

Facile electrochemical fabrication of nanostructured amorphous $Co(OH)_2$ on gold electrodes as an efficient oxygen evolution catalyst

16:10 to 16:30

Alexandr Simonov *(School of Chemistry, Monash University , Clayton, Australia)*, Alan Bond, Shannon Bonke, Thomas Gengenbach, Leone Spiccia

A.C. voltammetric water oxidation by metal oxides at low loadings: new mechanistic insights and riddles

16:30 to 16:50

Hidenori Yahiro *(Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, Matsuyama, Japan)*, Yoshiteru Itagaki

Improvement of Electrochemical Performance of Bilayer SOFC Electrodes Formed by EPD

16:50 to 17:10

Ramesh Kasi *(Physics, University of Malaya, Kuala Lumpur, Malaysia)*, Abdul Kariem Arof, Vengadaesvaran Balakrishnan, Ammar Saafamri, Ramesh Subramaniam

Electrochemical and Surface Analyses of Acrylic – Silicone - NanoSio$_2$ Based Nanocomposite Corrosion Protection Coatings

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Session 3

Room 3.404

Chaired by: Anthony Kucernak

13:50 to 14:20 Invited

Zhong-Qun Tian *(State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, China)*, Xiaoyu Cao, Xiaobing Ding, Yu Wang

Photoelectro-Catassembly of Two-dimensional Polymer

14:20 to 14:40

Pablo Fanjul Bolado *(R&D Department, DropSens, S.L., Oviedo, Spain)*, Alvaro Colina, Begoña González García, Aranzazu Heras, David Hernández Santos, Carla Navarro

Voltammetric reduction of graphene oxide and '*in situ*' Spectroelectrochemical characterization

14:40 to 15:00

Irina Svir *(Departement de Chimie, CNRS - Ecole Normale Superieure, Paris, France)*, Christian Amatore, Alexander Oleinick, Oleksii Sliusarenko

Validating a Central Approximation in Theories of Regular and Random Electrochemical Electrode Arrays

15:00 to 15:20

Philippe Hapiot *(Institut des Sciences Chimiques de Rennes, CNRS, Université de Rennes 1, Rennes, France)*, Benoit Boichard, Pascale Even-Hernandez, Cyrille Hamon, Yann Leroux, Sébastien Lhenry, Valérie Marchi

Electrochemical Investigations of Deposited Quantum Rods. Intrinsic Properties and Substrate Effects

15:20 to 15:50 Coffee Break

15:50 to 16:10

Yoon-Sok Kang *(Energy Lab, SAIT, Samsung Electronics, Suwon, Korea)*, Min Sik Park, Insun Park, Jun-Ho Park

Tetrathiafulvalene as a film forming additive for high-voltage lithium ion positive electrode

16:10 to 16:30

Michal Swietoslawski *(Faculty of Chemistry, Jagiellonian University, Krakow, Poland)*, Monika Bakierska, Marcin Molenda

Studies on solid-electrolyte interface in modified spinel systems for Li-ion batteries

16:30 to 16:50

Fu-Ming Wang *(Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei, Taiwan)*

Self Terminated Oligomer Branched Architecture (STOBA) in lithium ion battery

16:50 to 17:10

Bartosz Hamankiewicz *(Faculty of Chemistry, University of Warsaw, Warsaw, Poland)*, Mariusz Andrzejczuk, Maciej Boczar, Andrzej Czerwinski, Karol Fijalkowski, Michal Krajewski, Monika Michalska, Piotr Podsadni, Zbigniew Rogulski, Dominika Ziolkowska

Electrochemical properties of surface modified manganese-based powders for lithium-ion battery

Wednesday 20 April 2016 - Morning

Keynote

Theatre 1.439

Chaired by: Alison Downard

09:00 to 09:40 Keynote

Jadranka Travas-Sejdic *(Chemistry, The University of Auckland, Auckland, New Zealand)*

Polymer Brushes Grafted Conjugated Polymers for Biomedical Applications

Session 1

Room 3.402

Chaired by: Justin Gooding

09:50 to 10:10

Nihan Aydemir *(Chemistry, University of Auckland, Auckland, New Zealand)*, Clive W. Evans, Hazel McArdle, Selina Patel, Jadranka Travas-Sejdic, Whitney Whitford, David Williams

A Label-Free, Sensitive, Real-Time, Semiquantitative Electrochemical Measurement Method for DNA Polymerase Amplification (ePCR)

10:10 to 10:30

Jenny Malmstrom *(School of Chemical Sciences, University of Auckland, Auckland, New Zealand)*, Vaughan Feisst, Alissa J. Hackett, Jadranka Travas-Sejdic, David Williams

Grafted Conductive Polymer Surfaces for Switchable Electrochemistry and Modulation of Cell Adhesion

10:30 to 10:50

Adriana Ribeiro *(Chemistry and Biotechnology, Federal University of Alagoas, Maceio, Brazil)*, Andresa Almeida, Dimas Lima

Electrochromic Properties of a Magenta Polypyrrole Derivatised with Methyl Red

10:50 to 11:20

Coffee Break

11:20 to 11:50 Invited

NJ Tao *(Center for Bioelectronics and Biosensors, Arizona State University, Tempe, USA)*

Detecting small molecule-membrane protein binding kinetics

11:50 to 12:10

Lital Alfonta *(Life Sciences, Ben-Gurion University of the Negev, Beer-Sheva, Israel)*

Site-Specific vs. Non-Specific Wiring of Enzymes

12:10 to 12:30

Frédéric Barrière *(Institut des Sciences Chimiques de Rennes, Université de Rennes 1, Rennes, France)*

(Metallo)-Proteins and Enzymes in Bacteria at Modified Electrodes as Stable and Living Catalysts in Microbial Fuel Cells

12:30 to 12:50

Susana Cordoba de Torresi *(Instituto de Quimica, Universidade de São Paulo, São Paulo, Brazil)*, Aruã C. da Silva

Green synthesis of a biodegradable and conducting material for biomedical applications

12:50 to 13:00 **Farewell in Theatre 1.401**

Chaired by: Alison Downard and David Williams

Session 2

Theatre 1.401

Chaired by: Nick Birbilis

09:50 to 10:10

Xiaorong Gan *(School of Environmental Science and Technology, Dalian University of Technology, Dalian, China)*, Huimin Zhao

Understanding of Improved Electro-catalytic Activity of MoS_2 Nanosheets Synthesized by Liquid Phase Exfoliation

10:10 to 10:30

Aishui Yu *(Department of Chemistry, Fudan University, Shanghai, China)*, Yesheng Shang

Surface Modification of $LiMn_2O_4$ for Enhanced Performance at Elevated Temperature

10:30 to 10:50

Yue Ma *(Structural Chemistry, Department of Chemistry, Ångström Lab. Uppsala University, Uppsala, Sweden)*, Kristina Edström

Surface Modification Strategies for Silicon Anodes towards Very Robust Cycling upon Deep Lithiation

10:50 to 11:20

Coffee Break

11:20 to 11:50 Invited

Alan Bond *(School of Chemistry, Monash University, Clayton, Australia)*, Si-Xuan Guo, Yuping Liu, Jie Zhang

Electrocatalysis with Polyoxometalates

11:50 to 12:10

Maxi Frei *(IMTEK – Department of Microsystems Engineering, University of Freiburg, Freiburg, Germany)*, Lisa Dietel, Sven Kerzenmacher, Christian Köhler, Felix Wiedenmann

Highly Porous Electrodeposited Pt-Ru, Pt-Pd, and Pt-Au Electrodes for the Electro-Oxidation of Methanol, Formic Acid, and Glucose

12:10 to 12:30

Adam Lewera *(Department of Chemistry, University of Warsaw, Warsaw, Poland)*, Maciej T. Gorzkowski, Barbara Gralec

Carbon Monoxide, Formic Acid and Ethanol Electrooxidation on Pseudomorphic Noble Metal Layers and Nanoalloys

12:30 to 12:50

YuYe Tong *(Chemistry, Georgetown University, Washington, USA)*, De-Jun Chen

New Insights into Electrocatalysis of Methanol and Formic Acid Oxidation: from the Anodic vs Cathodic Peak Current Ratio Criterion to the Bifunctional Mechanism and to the Debate on the Intermediate

Session 3

Room 3.404

Chaired by: Conor Hogan

09:50 to 10:10

Zhi-Da Gao *(Department of Physics, College of Sciences, Northeastern University, Shenyang, China)*, Yan-Yan Song

Photocatalytical Synthesis of Prussian Blue Functionlized TiO_2 Nanotube Arrays: an Amperometric Sensing Platform for Glucose Detection

10:10 to 10:30

Nabin Aryal *(DTU Biosustain, Technical University of Denmark, Copenhagen, Denmark)*

Substantial Improvement of Chemical Production from Bio catalyzed Polymer Electrode in Bioelectrochemical System

10:30 to 10:50

Emmanuel Iwuoha *(SensorLab, Department of Chemistry, University of Western Cape, Cape Town, South Africa)*

Receptorsens and Endotek Signaling Systems for Estrogenic Endocrine Disrupting Chemicals (e-EDCs)

10:50 to 11:20 Coffee Break

11:50 to 12:10

Chun-Pei Cho *(Department of Applied Materials & Optoelectronic Engineering, National Chi Nan University, Nantou County, Taiwan)*

Photocatalytic activity of Ag-TiO_2-graphene ternary nanocomposites

12:10 to 12:30

Xiaojing Wang *(School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, China)*

Rare earth (Re=La, Ce, Eu, Tb) doped Ta_2O_5 materials and study on their electrocatalytic activity

12:30 to 12:50

Lin Lu (*Corrosion and Protection Center, University of Science and Technology Beijing, Beijing, China)*, Jin Gao, Xiao-gang Li, Min-na Yang

Influence of Magnetic Field on Interface Electrochemistry of Nickel-based Organic Coating

Poster Presentations

Poster presentation session on Monday 17:20 to 19:00

Poster Presentations

s1-001

Benjamin J. J. Austen *(Department of Chemistry, Nanochemistry Research Institute, Curtin University, Perth, Australia)*, Damien Arrigan

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

s1-002

Paul Baek *(School of Chemical Sciences, University of Auckland, Auckland, New Zealand)*, Nihan Aydemir, David Barker, Eddie Wai Chi Chan, Omer Chaudhary, Jenny Malmstrom, Jadranka Travas-Sejdic

Solvent vapour-induced healing of conducting polymer blends

s1-003

Soledad Bollo *(Pharmacological Sciences, University of Chile, Santiago, Chile)*

Reduced Graphene oxide improve the performance of glassy carbon electrodes against DNA and NADH detection

s1-004

Charlotte Carré *(PPME, University of New Caledonia, Noumea, France)*, Peggy Gunkel-Grillon, Marc Jeannin, René Sabot, Arnaud Serres

The calcareous deposit formed under cathodic polarization as a contaminant monitoring device in seawater

s1-005

Seulki Chae *(Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Jeong Beom Lee, Tae-jin Lee, Seung M. Oh, Ji Heon Ryu

Solid Electrolyte Interphase Generation *via* Surface-bonded Vinylene Carbonate on Graphite Negative Electrode for Lithium-ion Batteries

s1-006

Kwok Kiong Chan *(School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore)*, Richard D. Webster

Solid Phase Extraction - Voltammetric Coupled Detection of Caffeine in Acetonitrile

s1-007

Chun-Yi Chen *(Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan)*, Tso-Fu Mark Chang, Katsuyuki Machida, Kazuya Masu, Masato Sone, Daisuke Yamane, Masaharu Yoshiba

Pulse Electroplating of Ultra-Fine Grained Au Films with High Strength for Micro-Electrical-Mechanical System Devices

s1-008

Xinyi Chia *(School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore)*, Adriano Ambrosi, Jan Luxa, Martin Pumera, David Sedmidubský, Zdenek Sofer

Electrochemistry of Anti-MoS_2 structure: Tl_2S

s1-009

Xinyi Chia *(School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore)*, Adriano Ambrosi, Jan Luxa, Martin Pumera, Zdenek Sofer

Layered Transition Metal Dichalcogenides as Electrocatalysts for Hydrogen Evolution and Their Trends Emerging from Electrochemical Treatment

s1-010

Wan-Ting Chiu *(Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan)*, Tso-Fu Mark Chang, Chun-Yi Chen, Tomoko Hashimoto, Hiromichi Kurosu, Masato Sone, Yuma Tahara

Platinum Electroless Plating of Silk Utilizing Supercritical Carbon Dioxide

s1-011

Jung Sang Cho *(Department of Materials Science and Engineering, Korea University, Seoul, Korea)*

Hollow Nanosphere-Decorated Reduced Graphene Oxide Hybrid Nanofibers

s1-012

Zhihui Dai *(Department of Chemistry, Nanjing Normal University, Nanjing, China)*, Jing Li

Mn-Doped ZnO Nanorods Diluted Magnetic Semiconductor for Label-Free Photoelectrochemical Aptasensing

s1-013

Ashis Das *(Chemistry, Indian Institute of Technology, Madras, Chennai, India)*

Development of Sensitive Voltammetric Progesterone Sensor Using Micro-Rod Tin Modified Glassy Carbon Electrode in the Presence of Cetyltrimethylammonium Bromide Surfactant

s1-014

Thomas Doneux *(Chimie Analytique et Chimie des Interfaces, Université Libre de Bruxelles (ULB), Brussels, Belgium)*, Dan Bizzotto, Claudine Buess-Herman, Anne Meunier, Eleonore Triffaux

On the Use of *In Situ* Electro-Fluorescence Microscopy for the Study of Electrified Bio-Interfaces

s1-015

Alison Downard *(Department of Chemistry, University of Canterbury, Christchurch, New Zealand)*, Paula Brooksby, Haidee Dykstra, Anna Farquhar, Mark Waterland

Nitrophenyl Films on Few Layer Graphene (FLG): A Combined Electrochemistry, Spectroscopy and Microscopy Study

s1-016

Silviu Iulian Drob *(Electrochemistry and Corrosion, Institute of Physical Chemistry Ilie Murgulescu, Bucharest, Romania)*, Mihai Andrei, Jose Maria Calderon Moreno, Ioana Demetrescu, Cora Vasilescu

A Study of the Interface between a New CoCrNbMoZr Alloy and Artificial Saliva

s1-017

Silviu Iulian Drob *(Electrochemistry and Corrosion, Institute of Physical Chemistry Ilie Murgulescu, Bucharest, Romania)*, Mihai Anastasescu, Jose Maria Calderon Moreno, Petre Osiceanu, Monica Popa, Cora Vasilescu

Chemical Treatment of a new Ti-Zr-Nb Alloy Surface by Applying Hydroxyapatite Coating

s1-018

Ronggui Du *(Department of Chemistry, Xiamen University, Xiamen, China)*, Juan Hu, Yan Liang, Qing Liu, Hui Zhang

Fabrication of MoO_3 Nanoparticles Modified TiO_2 Nanotube Films for Photocathodic Protection of Stainless Steel

s1-019

Luigi Falciola *(Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy)*, Michele Ceotto, Giovanni Di Liberto, Guido Panzarasa, Valentina Pifferi, Guido Soliveri

The Silver Nanoparticles/TiO_2 Interface: a Combined Electrochemical and Theoretical Investigation

s1-020

Pablo Fanjul Bolado *(R&D Department, DropSens, S.L., Oviedo, Spain)*, Begoña González García, David Hernández Santos, Marta María Pereira Silva Neves

Non-enzymatic ethanol sensor based on a nanostructured disposable screen-printed electrode

s1-021

Anna Farquhar *(Deparment of Chemistry, University of Canterbury, Christchurch, New Zealand)*, Paula Brooksby, Alison Downard, Christopher Fitchett

Modifying Graphene *via* the Diels-Alder Reaction of an Anthranilic Acid: New Chemistry for Graphene Energy Storage Materials

s1-022

Bren Mark B. Felisilda *(Nanochemistry Research Institute / Chemistry Department, Curtin University, Perth, Australia)*, Eva Alvarez de Eulate, Damien Arrigan, J. Helen Fitton, Damien Stringer

Electrochemical Behaviour of Fucoidan Extracts from Seaweeds at a Polarized Water-Organogel Interface

s1-023

Zude Feng *(College of Materials, Xiamen University, Xiamen, China)*, Yingmin Liao

Electrochemically Induced Deposition of Enamel-Like Coating for Tooth Repair

s1-024

Bernhard Gollas *(Institute for Chemistry and Technology of Materials, Graz University of Technology, Graz, Austria)*, Salar Bozorgi, Daniel Schloffer

The Electrochemical Behaviour of Magnesium Alloys for Secondary Magnesium Ion Batteries

s1-025

Vinicius Goncales *(School of Chemistry, The University of New South Wales, Sydney, Australia)*, Leila Zarei, Moinul H. Choudhury, Roya Tavallaie, Stephen Parker, Simone Ciampi, Justin Gooding

Aiming the development of high-density DNA microelectrode arrays using light-activated electrochemistry

s1-026

Alissa J. Hackett *(School of Chemical Sciences, University of Auckland, Auckland, New Zealand)*, Julien E. Gautrot, Michael J. Higgins, Jenny Malmstrom, Paul J. Molino, Jadranka Travas-Sejdic, Gordon G. Wallace, David Williams, Hongrui Zhang

Conductive surfaces responsive to temperature and salt

s1-027

Mohammadamin Haghighatbin *(Department Chemistry and Physics, La Trobe University, Bundoora, Melbourne, Australia)*, Paul Burn, Conor Hogan, Shih-Chun Lo

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

s1-028

Yu Seok Ham *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Seunghoe Choe, Myung Jun Kim, Hoe Chul Kim, Soo-Kil Kim, Jae Jeong Kim

Fabrication of porous Au-Ag bimetallic electrocatalyst synthesized *via* electrodeposition for CO_2 reduction

s1-029

Joah Han *(Energy & Environmental Division, Korea Institute of Ceramic Engineering & Technology, Jinju-si, Korea)*, Kwang Chul Roh

Unzipped carbon nanotubes *via* KOH activation for high specific surface area and trimodal pore structure

s1-030

Katarzyna Hnida *(Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Krakow, Poland)*, Anna Gryszkiewicz, Dawid Karenda, Marcin Knutelski, Marek Przybylski, Grzegorz Sulka

Functional Hybrid Organic-Inorganic Nanomaterials Obtained *via* Cathodic Electrodeposition – Application in Energy Conversion and Electrosensing

s1-031

Zheng Huajun *(Department of Applied Chemistry, Zhejiang University of Technology, Hangzhou, China)*, Di Jing, Cheng Sanming, Zhao Zhefei

Solvothermal synthesis of carbon nanotubes@$NiCo_2O_4$ core-shell nanostructures as electrode material for supercapacitors

s1-032

Ghulam Hussain *(Nanochemistry Research Institute, Department of Chemistry, Curtin University, Perth, Australia)*, Debbie S. Silvester

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

s1-033

Jeemin Hwang *(Chemical and Biomolecular Engineering, Yonsei University, Seoul, Korea)*, Byungchan Han, Jin Goo Lee, Yong Gun Shul

A New Family of Perovskite Catalysts for OER in Alkaline Media: $BaNiO_3$, $BaNi_{0.83}O_{2.5}$

s1-034

Yota Ishizuka *(Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan)*, Tso-Fu Mark Chang, Chun-Yi Chen, Toshifumi Konishi, Katsuyuki Machida, Kazuya Masu, Masato Sone, Hiroshi Toshiyoshi, Daisuke Yamane, Sari Yanagida

Enhanced Mechanical Strength of Gold Electroplating Materials Fabricated by Multi-Layer Structure

s1-035

Paola Jara-Ulloa *(Departamento de Ciencias Químicas, Universidad Andres Bello, Santiago, Chile)*

GCE modified with carbon nanotubes : evaluation of dispersants agents for detection of M^{2+}

s1-036

Yongsoo Jeong *(Electrochemistry Lab, Korea Institute of Materials Science, Changwon, Korea)*, Joo-Yul Lee

Comparison of Al Electrodeposition at Different Solvents

s1-037

Hyoung-Joon Jin *(Department of Polymer Science and Engineering, Inha University, Incheon, Korea)*, Se Youn Cho, Young Soo Yun

Asymmetric Sodium-ion Supercapacitors with Faradaic Electrodes of Nanostructured Carbons

s1-038

Moon-Sung Kang *(Department of Environmental Engineering, Sangmyung University, Cheonan, Korea)*, Sung-Geun Cho, Do-Hyeong Kim, Chul-Gu Lee, Jin-Soo Park

Development of Pore-Filled Ionomer Membranes for Efficient Membrane Capacitive Deionization Application

s1-039

Colin Kang *(Chemistry, Curtin University, Perth, Australia)*

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

s1-040

Moon-Sung Kang *(Department of Environmental Engineering, Sangmyung University, Cheonan, Korea),* Sung-Geun Cho, Do-Hyeong Kim, Chul-Gu Lee, Jin-Soo Park

Performance Enhancement of Capacitive Deionization by Using Ionomer-Combined Carbon Electrodes

s1-041

Noah Kebede *(Department of Chemistry and Physics, La Trobe University, Bundoora, Australia)*, Gregory Barbante, Paul Francis, Conor Hogan

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

s1-042

Thomas Kerr-Phillips *(School of Chemical Sciences, the University of Auckland, Auckland, New Zealand)*, Frederic Vidal, Remy Agniel, Paul Kilmartin, Jenny Malmstrom, Giao Nguyen, Cedric Plesse, Jadranka Travas-Sejdic, Vincent Woehling

Electroactive Electrospun Semi-Interpenetrated Network Fibre Mats with Controllable Pore Sizes

s1-043

Roshan Khadka *(School of Chemical Sciences, The University of Auckland, Auckland, New Zealand)*, Nihan Aydemir, Jadranka Travas-Sejdic

Fast Responsive and High Performance PPy-PEO Conductive Polymer Actuators

s1-044

Hyun-Soo Kim *(Battery Research Center, KERI, Changwon, Korea)*, Min-Ki Jeon, Bong-Soo Kim

Electrochemical Performances of $Li_3V_2(PO_4)_3$ Cathode Materials for Li-Ion Battery

s1-045

Hyung-Tae Kim *(School of Chemical and Biological Engineering, Seoul National University, Seoul, Korea)*, Bonghyun Kim, Young Gyu Kim, Yoonjae Lee, Junyoung Mun, Seung M. Oh, Taeeun Yim

Non-flammable Binary Electrolytes for LIBs from Pyrrolinium-based Ionic Liquid and Carbonate

s1-046

Kang-Pil Kim *(Convergence Research Center for Solar Energy, DGIST, Daegu, Korea)*

Enhanced efficiency of dye-sensitized solar cells with trench structured TiO_2 nanoparticles photoelectrode

s1-047

Joo Hyun Kim *(WCD Department of Energy Engineering, Hanyang University, Seoul, Korea)*, Junghyun Choi, Ungyu Paik, Jihoon Seo, Seho Sun

Directly deposited PVP-Nafion nanofiber on sulfur cathode with enhanced electrochemical performance for lithium sulfur batteries

s1-048

Corinne Lagrost *(Institut des Sciences Chimiques de Rennes, CNRS and University of Rennes 1, Rennes, France)*, Andrea Mulas, Yves-Marie Hervault, Lucie Norel, Stéphane Rigaut

Electron Transfer Kinetics in Polymetallic carbon-rich Ruthenium(II) bis(σ-arylacetylides) Wires Connected to Gold

s1-049

Sherman J. L. Lauw *(School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore)*, Richard D. Webster, Xiuhui Xu

Primary Colored Electrochromism of 1,4-Phenylenediamines

s1-050

Jazreen H. Q. Lee *(School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, Singapore)*, Richard D. Webster

Electrochemistry of Pyridoxine (Vitamin B6) in Acetonitrile

s1-051

Jin-Young Lee *(Chemistry, Seoul National University, Seoul, Korea)*, Taek Dong Chung, Jae Gyeong Lee, Samuel Jaeho Shin

Electrochemical Deposition on Dielectric-Layered Electrode

s1-052

Dejun Li *(College of Physics and Materials Science, Tianjin Normal University, Tianjin, China)*, L. Dong, J. M. Feng, X. F. Li, G. Z. Wang

Facile Preparation Hybrid Material of $CoFe_2O_4$/graphene for Anode in Sodium Ion Batteries

s1-053

Dejun Li *(College of Physics and Materials Science, Tianjin Normal University, Tianjin, China)*, L. Dong, J. M. Feng, X. F. Li, G. Z. Wang

Graphene/Sb_2O_4 Nano-rod Hybrid Nanostructure for High-performance Sodium-ion Battery Anode

s1-054

Zonghuai Liu *(School of Materials Science and Engineering, Shaanxi Normal University, Xian, China)*, Wensheng Dong, Yibo He, Liping Kang, Chunling Liu

Holey graphene/PPy nanoparticle aerogels with three-dimensional hierarchical structure for high performance supercapacitor

s1-055

Yang Liu *(Australian Institute for Bioengineering and Nanotechnology, Brisbane, Australia)*, Xiaodan Huang, Chengzhong Yu

Nitrogen-doped Mesoporous Carbon Coated MWCNTs for Lithium Sulfur Batteries

s1-056

Yang Liu *(Department of Chemistry, Curtin University, Perth, Australia)*, Damien Arrigan, Alonso Gamero-Quijano, Grégoire Herzog, Angelika Holzinger, Peter Knittel, Christine Kranz, Lukasz Poltorak, William Rickard

Decoration of Liquid/Liquid Nanointerface Arrays with Silica for Visualisation of Diffusion Processes

s1-057

Gabriel Loget *(Institut des Sciences Chimiques de Rennes, Université of Rennes 1, Rennes, France)*, Sylvie Chardon, Bruno Fabre, Encarnacion Torralba-Penalver

Photoelectrocatalytic Reduction of CO_2 on Nanostructured Silicon Surfaces Using Molecular Catalysts Based on Metallic Complexes

s1-058

Subrata Mondal *(Chemistry, Indian Institute of Technology Madras, Chennai, India)*, M.V. Sangaranarayanan

Feasibility of Overoxidized Polyaniline towards Anion Exclusion Behavior and Sensing Applications

s1-059

Aravindan Natarajan *(Chemsitry, Indian Institute of Technology Madras, Chennai, India)*, M.V. Sangaranarayanan, Preethi Sankaranarayanan

Highly selective and non-enzymatic electrocatalytic detection of catechol using flower-like Cu particles modified Ppy coated GC electrode

s1-060

Tsuyoshi Ochiai *(Photocatalyst Group, Kanagawa Academy of Science and Technology, Kawasaki, Japan)*, Akira Fujishima, Mio Hayashi, Shoko Tago

A Novel Platinum-modified Titanium Electrode for Electrochemical Ozone Generation Prepared by the Multiple Electrostrike Method

s1-061

Eun-Suok Oh *(School of Chemical Engineering, University of Ulsan, Ulsan, Korea)*, Sangik Jeon, Boyeon Kim, Taewon Kim, Minh Hien Thi Nguyen, Yanchunxiao Qi

In-Situ Polymerization of Poly(acrylonitrile-butylacrylate)-Graphene Nanocomposite as a Promising Water-Based Binder for High Performance Lithium-ion Batteries

s1-062

Eun-Suok Oh *(School of Chemical Engineering, University of Ulsan, Ulsan, Korea)*, Soomyung Ha, Sangik Jeon, Boyeon Kim, Ketack Kim, Seul Lee, Minh Hien Thi Nguyen

Effect of emulsified binders on the performance of carbon electrochemical double-layer capacitors

s1-063

Ruchika Ojha *(School of Chemistry, Monash University, Clayton, Australia)*, Stephen Best, Alan Bond, Glen Deacon, Peter Junk

Fate of a monomeric Pt^{III} species produced *via* electrochemical oxidation of anticancer compound trans-$[Pt^{II}\{(p\text{-}BrC_6F_4)NCH_2CH_2NEt_2\}Cl(py)]$

s1-064

Sachiko Ono *(Department of Applied Chemistry, Kogakuin University, Tokyo, Japan)*, Hidetaka Asoh, Atsushi Kiyotake, Akira Komatsu, Hideki Monma

Effects of Nanostructure and Composition of Anodic Oxide Films on Growth of Apatite by Alternative Immersion Method

s1-065

Tommi Palomäki *(Department of Electrical Engineering and Automation, Aalto University, Espoo, Finland)*, Jeon Geon Han, Leena-Sisko Johansson, Jari Koskinen, Tomi Laurila, Timo Sajavaara, Niklas Wester

Effect of Power Density and Doping on the Electrochemical Properties of Nanocrystalline Carbon (nc-C) Thin Films

s1-066

Jin-Soo Park *(Department of Environmental Engineering, Sangmyung University, Cheonan, Korea)*, Sung-Geun Cho, Jang-Uk Choi, Ye-Jin Jeong, Moon-Sung Kang, Da-Eun Kim, Chul-Gu Lee, Chan-Ho Song

Porous Carbon Electrodes for Non- and Faradaic Reactions

s1-067

Jin-Soo Park *(Department of Environmental Engineering, Sangmyung University, Cheonan, Korea)*, Sung-Geun Cho, Ye-Jin Jeong, Moon-Sung Kang, Chul-Gu Lee, Mun-Sik Shin

Effect of Surface Pretreatment of Dimensionally Stable Anodes on the Performance of the Anodic Reactions

s1-068

Valentina Pifferi *(Dipartimento di Chimica, Università degli Studi di Milano, Milan, Italy)*, Luigi Falciola, Guido Panzarasa, Guido Soliveri

Electrochemistry Provides Better Understanding of Polymer Brushes as Smart Coatings

s1-069

Kwang Chul Roh *(Energy & Environmental Division, Korea Institute of Ceramic Engineering & Technology, Jinju-si, Korea)*, Ji Su Chae

Surface Modified $LiNi_{0.5}Mn_{1.5}O_4$ by Li_2O-$2B_2O_3$ for Lithium-ion Batteries

s1-070

Mahsa Saeedi Maleki *(Department of Chemistry and Physics, La Trobe University , Melbourne, Australia)*, Conor Hogan

Low Cost Sensing of Pseudoephedrine with Electrochemiluminescence Detection Using Mobile Phone

s1-071

Jihoon Seo *(WCD Department of Energy Engineering, Hanyang University, Seoul, Korea)*, Jinok Moon, Ungyu Paik

Control of localized galvanic corrosion between tungsten and titanium nitride during chemical mechanical planarization

s1-072

Shaomin Shuang *(Department of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, China),* Chuan Dong, Congli Wang

Ultra-sensitive detection for tryptophan based-on β-cyclodextrin conjugated magnetic graphene oxide modified glassy carbon electrode

s1-073

Paulina Sierra-Rosales *(Departamento de Química Organica y Fisicoquimica, Universidad de Chile, Santiago, Chile),* J. Arturo Squella, Carla Toledo-Neira

Determination of Food Dyes in Soft Drinks Using MWCNT modified GCE

s1-074

Neso Sojic *(ISM - ENSCBP, University of Bordeaux, Pessac, France)*, Stéphane Arbault, Laurent Bouffier, Anne de Poulpiquet, Alexander Kuhn, Dragan Manojlovic, Milica Sentic

From Light-Emitting Bioswimmers to 3D Electrogenerated Chemiluminescence

s1-075

Neso Sojic *(ISM - ENSCBP, University of Bordeaux, Pessac, France)*, Stéphane Arbault, Luigina De Leo, Henok Habtamu, Dragan Manojlovic, Tarcisio Not, Milica Sentic, Morena Silvestrini, Paolo Ugo

A Sensitive Electrochemiluminescence Immunosensor for Celiac Disease Diagnosis Based on Nanoelectrode Ensemble

s1-076

Youngsup Song (*Electrochemistry, Korea Institute of Materials Science, Changwon-si, Korea)*, Sung Mook Choi, Kyu Hwan Lee, Joo Yul Lee, Jae-Hong Lim

Lead Selenide Nanoribbons Synthesized by Galvanic Replacement of Lithographically Patterned Nickel Electrodes

s1-077

Juan Squella *(Department of Organic and Physical Chemistry, University of Chile, Santiago, Chile)*, Elizabeth Inostroza, Raul Moscoso

Voltammetric study of poli-nitrocompounds encapsulated in MWCNT electrode

s1-078

Ulrich Stimming *(School of Chemistry, Newcastle University, Newcastle upon Tyne, United Kingdom)*, Jing-Ying Gu, Max Herpich

Imaging and Electrochemical Investigation of DNA structures on HOPG Using Scanning Probe Microscopy

s1-079

Bradley Stringer *(Dept. of Chemistry and Physics, La Trobe University, Melbourne, Australia*), Peter Barnard, Conor Hogan, Linh Quan

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

s1-080

Yan Su *(School of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing, China)*, Ying Wan, Pengjuan Wang

Aptamer-Initiated On-Particle Template-Independent Enzymatic Polymerization (aptamer-OTEP) for Electrochemical Analysis of Tumor Biomarkers

s1-081

Yongsug Tak *(Chemical Engineering, Inha University, Incheon, Korea)*, Sangwon Choi, Gibaek Lee

Effects of Aluminum Surface Properties on the Cycleability of Al-ion Battery

s1-082

Haochun Tang *(Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan)*, Tso-Fu Mark Chang, Chun-Yi Chen, Katsuyuki Machida, Kazuya Masu, Masato Sone, Daisuke Yamane

Preparation and Characterization of Gold Films by Electroplating with Supercritical Carbon Dioxide

s1-083

Minami Teranishi *(Precision and Intelligence Laboratory, Tokyo Institute of Technology, Yokohama, Japan)*, Tso-Fu Mark Chang, Chun-Yi Chen, Toshifumi Konishi, Katsuyuki Machida, Kazuya Masu, Masato Sone, Hiroshi Toshiyoshi, Daisuke Yamane

Mechanical Characteristics of Structure Stability with Ti/Au Micro-Cantilevers Formed by Au Electroplating

s1-084

Malcolm Tessensohn *(Division of Chemistry & Biological Chemistry, Nanyang Technological University, Boon Lay, Singapore)*, Hajime Hirao, Richard Webster

Using the Electrochemistry of Phenylenediamines as a Measure of the Hydrogen Bonding Abilities of Alcohols in Organic Solvents

s1-085

YuYe Tong *(Chemistry, Georgetown University, Washington, USA),* De-Jun Chen, Eric G. Sorte

New Operando Methods for Fuel Cells and Batteries: Dual-Electrode IR Spectroscopy and Stripline NMR spectroscopy

s1-086

Seiya Tsujimura *(Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan)*, Aimi Suzuki

Hofmeister Effects on Glucose Oxidase-Redox Hydrogel Electrode

s1-087

Guntars Vaivars *(Chemistry, University of Latvia, Riga, Latvia)*, Andris Zicmanis

The Water Impact on Interface Metal Electrode/ Ionic Liquid as Studied by Impedance Analysis

s1-088

Cora Vasilescu *(Electrochemistry and Corrosion, Institute of Physical Chemistry Ilie Murgulescu, Bucharest, Romania)*, Jose Maria Calderon Moreno, Ioana Demetrescu, Silviu Iulian Drob, Monica Popa, Aurora Salageanu, Ecaterina Vasilescu

Functionalisation of new Ti-Zr-Ta-Ag alloy surface by deposition of anti-bacterial nanoparticles

s1-089

Cora Vasilescu *(Electrochemistry and Corrosion, Institute of Physical Chemistry Ilie Murgulescu, Bucharest, Romania)*, Mihai Anastasescu, Jose Maria Calderon Moreno, Silviu Iulian Drob, Petre Osiceanu, Monica Popa

Modification of the new Ti-Ta-Zr alloy surface by electrodeposition. Electrochemical and structural characterization of obtained nanolayer

s1-090

Ying Wan *(School of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing, China)*, Yan Su, Pengjuan Wang

TdT initated Supermolecular DNA Network on Electrode Surface

s1-091

Guangyuan Xu *(School of Chemical Sciences, PERC University of Auckland, Auckland, New Zealand)*

Light scribe graphene and conducting polymers for generating a new, high-performance electrochemical electrode

s1-092

Claudia Yañez *(Organica y Fisicoquimica, Universidad de Chile, Santiago, Chile)*

Immobilization of Cyclodextrin on Gold Electrode Based on Bottom-Up Approach

s1-093

Chun-Chen Yang *(Chemical Eng., Ming Chi University of Technology, New Taipei City, Taiwan)*

Enhanced high temperature performance of $LiFe_{0.5}Mn_{0.5}PO_4/C$ cathode materials *via* surface modification

s1-094

Chun-Chen Yang *(Battery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City, Taiwan)*, Yi-Wen Chen

Study of electrochemical performance of $LiFe_{0.5}Mn_{0.5}PO_4/C$ composite cathode doped with yttrium and chloride

s1-095

Chun-Chen Yang *(Battery Research Center of Green Energy, Ming Chi University of Technology, New Taipei City, Taiwan)*, Cheng-En You

High electrochemical performance of surface-modified $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ cathode materials

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Electrochemical Sensing Based on Modified Interfaces and Analytical Instrument-Integrated Applications

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Preparation and characterization of three-dimensional nanoporous carbon from expanded graphite for high energy density supercapacitor in aqueous electrolyte

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In this work, we present the synthesis of low cost carbon nanosheets derived from expanded graphite dispersed in Polyvinylpyrrolidone, subsequently activated in KOH and finally carbonized in Ar atmosphere. Interconnected sheet-like structure with low concentration of oxygen (9.0 at.%) and a specific surface area of 457 m^2 g^{-1} was obtained. The electrochemical characterization of the carbon material as supercapacitor electrode in a 2-electrode configuration shows high specific capacitance of 337 F g^{-1} at a current density of 0.5 A g^{-1} as well as high energy density of 37.9 Wh kg^{-1} at a power density of 450 W kg^{-1}.This electrical double layer capacitor electrode also exhibits excellent stability after floating test for 120 h in 6 M KOH aqueous electrolyte. These results suggest that this activated expanded graphite (AEG) material has great potential for high performance electrode in energy storage applications.

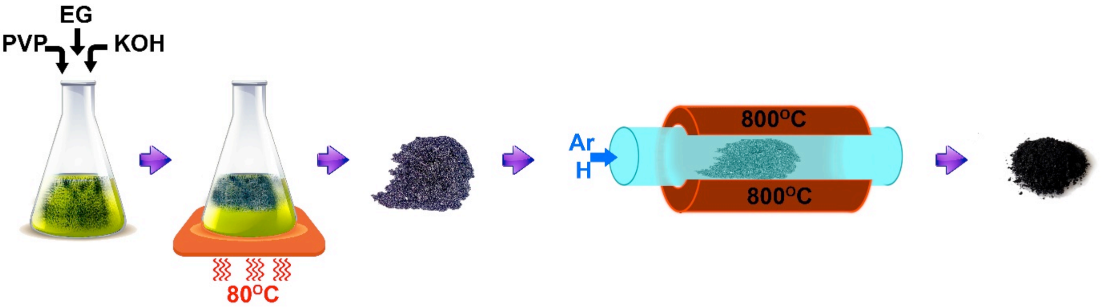

Fig. 1. Schematic diagram of the preparation process of AEG

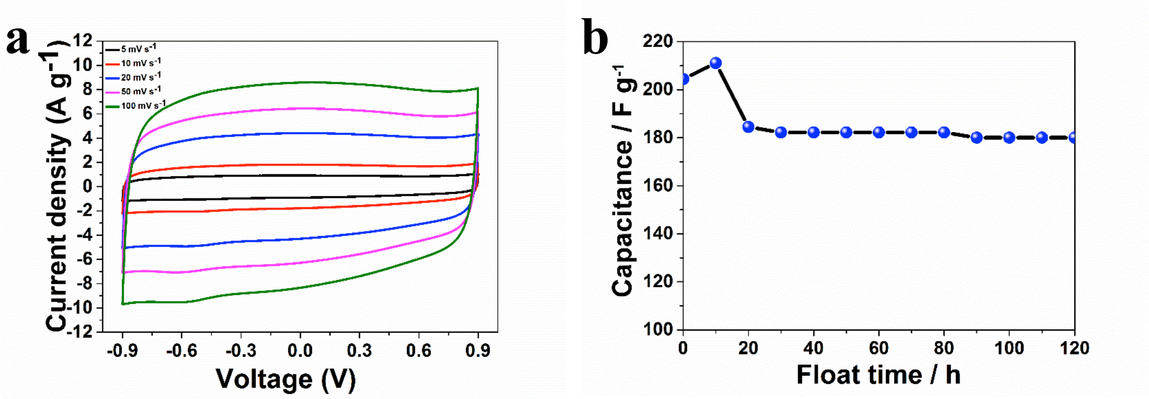

Fig. 2. (a) CV curves at scan rates from 5 to 100 mV s^{-1}, (b) voltage holding vs. capacitance at a constant current density of 1 A g^{-1}

Electrochemical catalytic oxidation of biphenol A on ferric hydroxide colloidal particle modified carbon paste electrode studied by cyclic votammetry and PM7 semi-empirical molecular orbital method

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In this presentation, graphite powder surface was modified with ferric hydroxide colloidal particles. The modified graphite powder was mixed with methyl silicone oil to make up a carbon paste electrode (CPE). The modified CPE not shows a liquid phase micro extraction to biphenol A in the methyl silicone oil from aqueous solution (compared with carbon electrode with same geometric area, small potential negative shift and larger oxidation peak current increase for about 5.5 times), but also the electrochemical catalytic oxidation to biphenol A with the catalyst of ferric hydroxide colloidal particles (compared with the unmodified CPE, larger oxidation potential shift 0f of 0.25 V and increase in oxidation peak current about 46% increase) shown in Fig.1. The quantum chemical calculation was performed with PM7 semi-empirical molecular5 orbital method in mopac2012 software with molecular clusters composed of a graphene sheet with 38 carbons, ferric hydroxide and biphenol A. the calculation results were analysis with thermodynamics shown the stability of the molecular clusters and molecular descriptors of exchangeable electrons, which shown 30% increase of the exchangeable electron in modified CPE compare with that of unmodified CPE. The calculation results also shown that the LUMOs of the modified and unmodified CPEs are composed of πorbital from graphene sheet, indicated electron transfer from molecular HOMO to electrode material of graphite powder. The HOMOs of unmodified and modified CPE with biphenol A are composed of p, d atomic orbitals from graphene, ferric hydroxide and biphenol A. Compare with frontier orbital energy gap of 8.938 eV of biphenol A, the energy gap of the frontier orbital is reduced to 5.241 eV for unmodified CPE and to 5.087 eV for modified CPE, which is correspondence for the catalytic behavior of biphenol A in the modified CPE as shown in Fig.2.

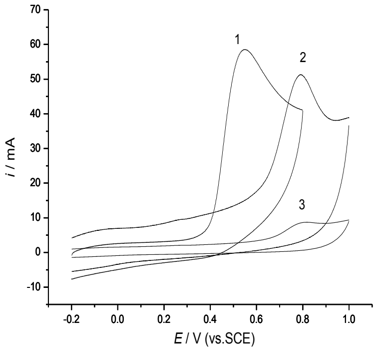

Fig.1 Cycli votammograms of biphenol A at modified CPE (1), unmodifie CPE (2) and carbon electrode (3). Scan rate 100mV.s^{-1} in pH8.0 0.20 M KCl solution.

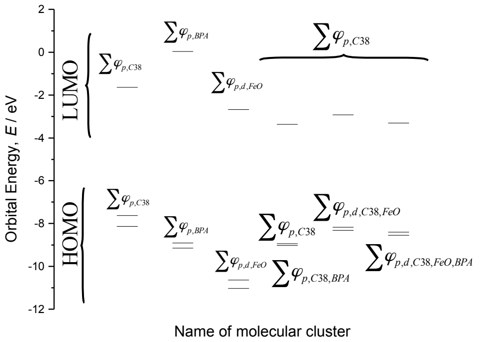

Fig. 2 the frontier orbitals of one LUMO and two HOMOs of molecular clusters and molecules with energy, energy gap

Exfoliated MoS_2 and ionic liquids for catalysis of CO_2 electro-reduction

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Carbon dioxide is the primary greenhouse gas emitted from human activities and its increasing concentration in the atmosphere is causing adverse effects on global climate. Recent efforts have shown the feasibility of converting it into valuable products and fuels via electrochemical reduction [1] However, high overpotentials are required for that, making necessary the design of catalytic systems. MoS_2 is a 2D layered material that has been intensely studied as catalyst for hydrogen evolution reaction (HER) [2]. Its catalytic sites are located at the edge planes, being its basal planes inert. In addition, this is a semiconducting material and its poor electron transport can limit the catalytic activity. Recent studies have shown that structural changes from the semiconducting 2H to the metallic 1T form takes place when MoS_2 layers are exfoliated, increasing its transport properties. Moreover, upon exfoliation, the main active sites are no longer at the edges, been the sites at the basal planes also active for HER [2]. In this study, we propose the use of exfoliated MoS_2 as catalyst for the CO_2 reduction. Previous reports have shown that the edge plane of such materials at its crystal form can be active for such reaction [3,4]. We synthetized large MoS_2 single crystals with preferable grown along the plane that can give rise to large sheets upon exfoliation. These sheets can be further broken down under sonication. Small and large sheets were studied as catalyst using either methanol or $BMImBF_4$ as the proton source in a DMF-based electrolyte. The proton source promotes the CO_2 reduction reaction via a mechanism that avoids the formation of a radical intermediate, reducing the equilibrium potential. However, it can compromise the selectivity once the CO_2 reduction reaction will compete with HER.

The results have shown that both reduction of CO_2 to CO and HER happen under these conditions. With the small sheets, 75% efficiency in achieved for CO formation when the ionic liquid is employed as the proton source, while only H_2 is observed as the product when the source of protons is methanol. It is believed that the BMI^+ cation adsorbs at the surface of the MoS_2 hindering the adsorption and binding of H^+. Moreover, imidazolium cations can capture CO_2 molecules facilitating its reduction. Selectivity for CO formation is considerably lower (13%) with the larger MoS_2 sheets, even with the ionic liquid as the proton source, which is probably due the fact that the basal plane is active for HER but not for CO_2 reduction.

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Electrodeposition of tin(II) from acid chloride solutions by using a membrane cell

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Abstract: Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CHR) in combination with galvanostatic electrolysis have been performed to investigate the electrodeposition of tin(II) from acid chloride solutions by using a membrance cell. The application of a membrane cell is efficient in improving solution stability, electrolytic efficiency and deposit morphology. Cyclic voltammograms at different scan rates reveal that the reduction process of tin(II) is likely to be irreversible and diffusion-controlled. Furthermore, a limiting cathodic polarization could be achieved under appropriate temperature (308 to 318 K), suitable H^+ concentration (3.5 to 4.5 mol L^{-1}), enough Sn^{2+} concentration (more than 20 g L^{-1}). The chronoamperometry measurement exhibits that the initial tin electrodeposition process follows an three-dimensional nucleation and subsequent grain growth mechanism limited by diffusion. Moreover, the proton reduction occurs in parallel with the electrodeposition of tin. Galvanostatic electrolysis experiments indicate that the tin deposit obtained at the cathode current density of 200 A m^{-2} is the best uniform, compact and present (220) preferred orientation. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

Calixarene Assembly With Enhanced Photocurrents Using $P(SNS-NH_2)/CdS$ Nanoparticles Structure Modified Au Electrode Systems

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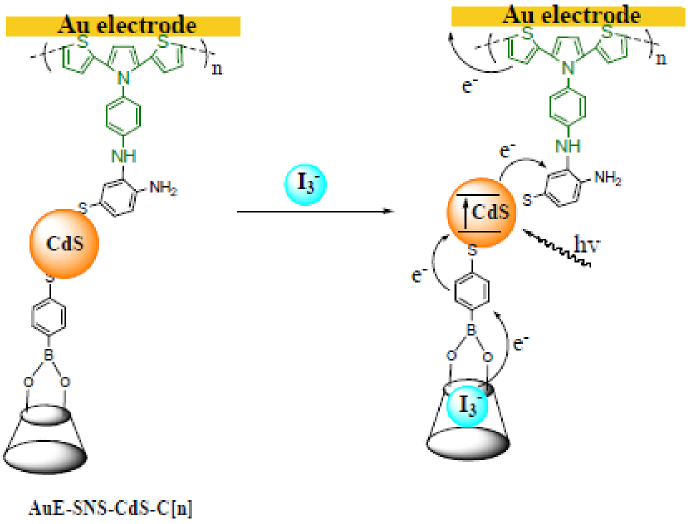
Two novel calix[n]arene-adorned gold electrodes producing high photocurrent intensities were successfully constructed by embedding gold electrode surfaces with both P(4-(2,5- di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine) conducting polymer and 4-mercaptoboronic acid-functionalized semiconductor CdS nanoparticles to facilitate the binding of calix[n]arene sulfonic acids with nanoparticles. This structure enabled an electron transfer cascade that both induced effective charge separation and efficiently generated photocurrent. The prepared electrodes were used to generate photocurrent by relying on the host-guest interactions of guests Br_3^- and I_3^-, which if positioned well in the system was able to fill electron-hole pairs of CdS nanoparticles. As a result, host calixarene derivatives crucially held Br_3^- and I_3^- ions at a substantial distance from CdS nanoparticles. Furthermore, the effects of various calixarenes on the photocurrent obtained indicate that the system's generation of photocurrent intensities depends on the cavity sizes of calixarene derivatives, which provide an essential center for Br_3^- and I_3^- ions (Scheme 1) [1].



Scheme 1. Generation of photocurrent by the AuE-P(SNS-NH2)-CdS-Calix[n]arene in the presence of I_3^- ion.

Acknowledgements

The Authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK Grant Number 109T439) for the financial support of this research.

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Enzyme Immobilization In Biosensor Constructions: Self-Assembled Monolayers Of Calixarenes Containing Thiols

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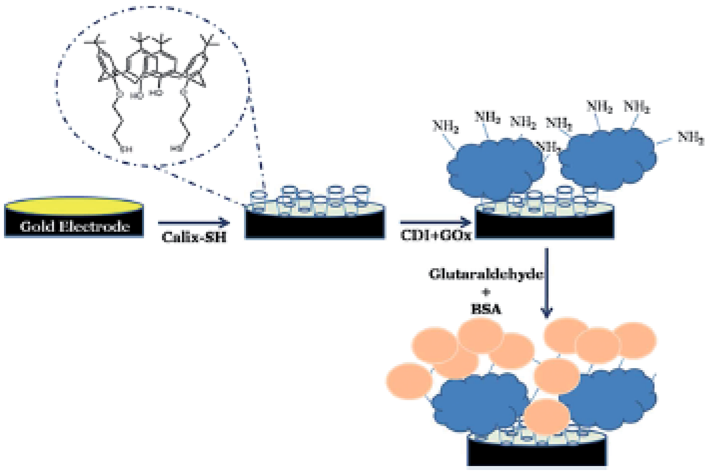
Herein, an amperometric glucose oxidase (GOx) biosensor is presented using calixarenes as an immobilization matrix of the biomolecule. Firstly, thiol-containing calixarenes (Calix-SH) were synthesized, then self-assembled monolayers (SAMs) of Calix-SH on a gold surface were formed and hydroxyl groups of Calix-SH were activated using 1,1′-carbonyldiimidazole (CDI) chemistry. To test the usability of Calix-SH modified surfaces as a biosensor, glucose oxidase was used as a model biological component. After optimization of preparation and working conditions, our results indicate that the Calix-SH/GOx biosensor has a linear range in the range 0.1–1.0 mM (LOD: 0.015 mM) for glucose with a 25 s response time. Finally, the application of the biosensor was examined to detect glucose in real samples. The glucose amounts were calculated as 19.460 ± 0.521 and 31.647 ± 2.125 mM in coke and fizzy drink (with orange), respectively. To confirm the reliability of the Calix-SH/GOx biosensor, the calculated glucose concentrations which were analyzed by the Calix-SH/GOx biosensor were compared to conventional spectrophotometric glucose kits. The glucose amounts in coke and fizzy drink were calculated as 18.509 ± 0.732 mM and 31.579 ± 4.466 mM, respectively [1]



Scheme 1. Schematic representation of Calix-SH/GOx biosensor.

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The Authors would like to thank the Scientific and Technological Research Council of Turkey (TUBITAK Grant Number 113T022) for the financial support of this research.

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Detection of Tuberculosis (Human and Bovine)

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Tuberculosis is a highly infectious disease caused by mycobacterium tuberculosis. Traditional methods of diagnosis such as chest X rays and sputum smear microscopy are expensive and lengthy making them unsuitable for developing countries. We have developed a method of printing mycolic acids onto nitrocellulose membranes and gold coated electrodes. These compounds are found on the cell walls of mycobacteria and are capable of binding to TB positive antibodies. Sera can then be added allowing any positive antibodies to bind, a secondary antibody conjugated to gold nanoparticles is then added which bind to any TB antibodies on the surface giving a colored spot as a sign of a positive result or an increase in impedance. As this test detects lipid antibodies it will also be able to detect TB in patients co-infected with HIV. This test is simple to run, takes only half an hour and importantly is under $5. It is thought that this approach could be used to detect other non-tuberculosis mycobacterial infections such as Buruli Ulcers and Leprosy by using a range of mycolic acids.

Modification of Ti Surfaces with Gradients of TiO_2 Nanotubes by Bipolar Anodization

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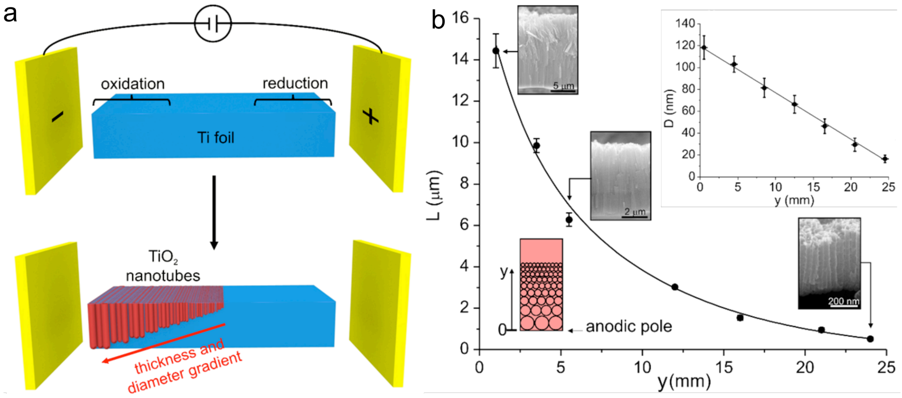
Arrays of self-organized TiO_2 nanotubes (TiO_2 NTs) grown on Ti by electrochemical anodization attract a huge scientific interest.[1] Due to the electronic properties and the biocompatibility of TiO_2, these one-dimensional nanostructure arrays are highly promising for applications in the fields of dye-sensitized solar cells (DSSCs), water splitting, photocatalysis and biomedical devices.[1]



a) Scheme showing the principle of bipolar anodization for the fabrication of TiO_2 NT gradients.[3] b) Length and diameter (inset) profile of a TiO_2 NT gradient.[4]

Bipolar electrochemistry is a phenomenon currently attracting a considerable attention in the domains of materials science and analytical chemistry.[2] It is based on the polarization of conducting object in electric fields which allows the generation of redox reactions on the surface of conductive objects without the use of electric wires. In this contribution, we report the use bipolar electrochemistry coupled to anodization for the rapid and wireless fabrication of self-assembled TiO_2 NT layers that consist of highly defined and controllable gradients in NT length and diameter.[3] The screening of these gradients is then used for finding the tube dimensions which are optimal for providing optimal photocurrents or H_2 production on dye-impregnated or Pt-modified TiO_2 interfaces. The development of this fabrication technique could allow reducing considerably the time for the optimization of TiO_2 NTs-based devices such as solar cells or photoelectrochemical water splitting devices.[3,4]

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Etching Treatment of Vertically Plate-like WO_3 Array as Photoanode for Enhanced Photoelectrochemical Performance

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Abstract

Photoelectrochemical(PEC) water splitting using semiconductor thin film as a desirable and environmental way to obtain clean energy, has attracted considerable attention since 1972[1]. For the overall water splitting reaction involving two half reaction, oxidation half reaction being four electron process is the slower one. Hence, development of efficient photoanodes for water oxidation is a critical subject. WO_3 is one of the best candidates as photoanode due to its suitable band (2.5 eV~2.8 eV), high electron mobility (~12 $cm^2V^{-1}S^{-1}$), long hole diffusion length (~150 nm) and stability against photocorrsion. It has been reported vertically aligned WO_3 with fewer grain boundaries offers an effective channel for the directional transfer of electrons. On the other hand, the monoclinic WO_3 with (002), (200) and (020) facets show a much higher photocatalytic O_2 evolution [2,3].

In this work, we report a vertically plate-like WO_3 array derived from one-step hydrothermal method using citric acid as structure-directing agent without the assistance of seed layer under mild temperature. A directing etching treatment using thiacetamide was followed to obtain rough surface with small pores. The structure and morphologies of as-prepared materials were analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). It was found the intensity of (002) and (020) facets belong to monoclinic WO_3 improved compared to the pristine one. The obtained photoanode exhibited an enhanced photocurrent density of□1.2 mA/cm^2 at 1.2 V vs Ag/AgCl, compared to 0.97 mA/cm^2 of pristine WO_3.

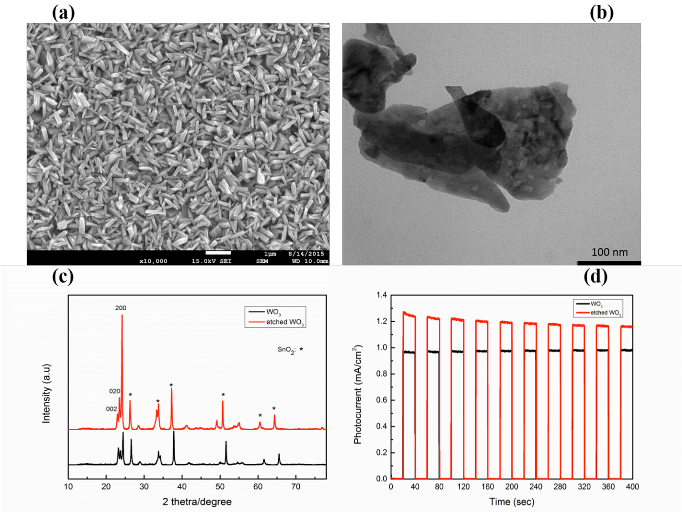

Fig 1. SEM of pristine WO_3(a), TEM of etched WO_3(b), XRD of as-synthesized samples(c), Photocurrent density curves of WO_3 samples(d)

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Composite membrane for redox flow battery

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With the expanding need for large electrical energy storage systems in connection with renewable energy sources, flow batteries, have been enormously considered due to their high flexibility in upgrade and low cost associated with scale-up. Of all the flow batteries, vanadium redox flow battery (VRFB) use of same element in both half-cell solutions that overcomes the inherent issue of cross contamination by diffusion of different ions across the membrane. Together with the absence of any toxic emissions, the vanadium redox flow battery has demonstrated its uniqueness in terms of safety and long life cycle. Typical charge-discharge reactions of a VRFB involve two vanadium redox couples, V(II)/V(III) and V(IV)/V(V), in the negative and positive half-cells, respectively. In a fashion similar to most batteries, electrons are transferred between the two electrodes through the external circuit during the charge and discharge processes. In a VRFB, the ion exchange membrane is a key component as an ionic conductor and separator: it not only provides an ionic conduction pathway between the two electrolytes but also prevents mixing of the negative and positive electrolytes. The crossover of ions through the membrane, with the diffusion of vanadium ions from one half-cell to the other due to the concentration gradients between the two electrolytes, will result in self-discharge and thus the loss of the chemical energy.

In this study, the composite membrane of hydrocarbon polymer with perfluorinated organic membrane were fabricated and characterized in terms of ionic conductivity and permeability. The ionic conductivity was measured with four point probe method and the permeability was measured with UV spectroscopy. The composite membrane exhibited comparable ionic conductivity with perfluorinated organic membrane and 30 – 40 % lower permeability than perfluorinated organic membrane. With performances of VRFBs, the energy efficiencies of VRFBs will be discussed.

Ionic Liquids as Electrolytes for Electrochemical Double Layer Capacitors

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Electrochemical double-layer capacitors (EDLCs) are a class of energy storage devices known for their high-power densities (up to 10 $kWkg^{-1}$).[1] Their ability to accept or deliver charge at substantially higher rates than electrochemical cells suitable for use in applications where peak demand is substantially greater than the average load.[2] Other desirable features of EDLCs are that they possess long cycle life (in excess of 500000 cycles) and relatively high energy efficiencies.[3] Consequently, EDLCs can be used to produce systems that require less maintenance than those where energy is stored in batteries. Conventional EDLCs are comprised of activated carbonbased electrodes, an electrically insulating separator, and an organic electrolyte solution.[3] The electrolyte is typically a solution of tetraethylammonium tetrafluoroborate in acetonitrile or propylene carbonate, restricting the use of EDLCs at higher operating temperatures. Ionic liquids (ILs) have received a significant degree of attention as an alternative to organic electrolytes, not only for EDLCs but also for lithium ion batteries. They are considered to be less hazardous than conventional electrolytes due to their nonflammable nature and the fact that they tend to exhibit negligible vapor pressures. The structure of these components and their degree of coordination have substantial influence over the physical properties of ILs, with the nature and relative sizes of the ions being known to strongly influence viscosity. This in turn affects ionic conductivity, which is a crucial parameter in the design of EDLCs as it has a profound influence on the equivalent series resistance (ESR) of the cells. A wide ESW is a characteristic frequently associated with ILs, which is also of benefit to their application as EDLC electrolytes. The energy stored in an EDLC, E, can be determined using the relationship $E = 1/2\ CV^2$, where C represents the cell capacitance and V the operating voltage of the cell. The maximum power output, Pmax, is governed by the relationship, $P_{max} = V^2/(4 \times ESR)$, where ESR represents the equivalent series resistance of the device. Therefore, the operating voltage, which is limited by the electrochemical stability of the electrolyte, significantly influences the energy and power densities attainable in EDLCs.

In this work, we investigate the behavior of ionic liquids containing sulfonium cations as electrolytes for EDLCs. Physical properties such as viscosity and ionic conductivity were reported over a range of temperatures, as well as their thermal and electrochemical behavior. The S-ILs were shown to exhibit relatively low viscosities and high ionic conductivities (with their relative performance being related to the size and structure of the cation); however, they also exhibited limited electrochemical stability resulting in an operating voltage of 2.5 V. The electrochemical performance of the S-ILs was not found to relate to any physical property in a simple manner. For example, $[S_{222}][Tf_2N]$ displays the highest ionic conductivity and lowest viscosity, which are desirable traits for an electrolyte but exhibits comparable performance in terms of specific capacitance with $[Pyr_{14}][Tf_2N]$, which contains a larger cation and exhibits low ionic conductivity and high viscosity. The unusual behavior of $[S_{223}][Tf_2N]$, which displays relatively high specific capacitances at low rates but substantially diminished performance at higher rates, was attributed to the existence of aggregated ions that are unable to participate in charge storage at higher rates. This ionic coordination is evident when viscosity and conductivity are expressed in the form of a Walden plot, where $[S_{223}][Tf_2N]$ displays a significantly different gradient to the other ILs. In conclusion, this work shows that $[S_{221}][Tf_2N]$ can perform better as an EDLC electrolyte than $[Pyr_{14}][Tf_2N]$ at room temperature, despite operating at a lower potential. It is also clear that despite exhibiting desirable traits such as relatively high ionic conductivity and low viscosity, enhanced electrochemical stability can outweigh some of the limitations associated with IL electrolytes in terms of energy and power.

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Halidated Carbons for Hybrid Electrochemical Supercapacitors: Interface Analysis for Faradaic Activity

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Electrochemical double layer capacitors (EDLC) are a special class of energy storage device delivering excellent power density. These supercapacitors (or ultracapacitors) broadly employ activated carbons using non-faradaic double layer capacitance and/or metal oxides (e.g. MnO_2/RuO_2) using faradaic activity (charge-transger). Activated carbon has long dominated the former category, where the net capacitance can be improved solely by morphology engineering i.e. (i) by increasing the overall surface area and (ii) tuning the porosity in the micropore regime. My research effort has demonstrated the overall volumetric energy density of activated carbon can be significantly improved by combining both high surface area morphology as well as chemical modification at interface. Using chemical halidation, modified carbon-halide [$C:X_n$; X = I, Br] nanocomposites can be obtained [1-5]. These electrogenative halides (I_2/ Br_2) induce charge transfer reaction at the interface while creating polyiodide ($C:I_3$/ $C:I_5$) or polybromide ($C:Br_3$) species particularly filling the interfacial micropores (0-2 nm) leaving the large mesopores (2-50 nm) open. In the current presentation, I will focus on the chemical halidation mechanism at the activated carbon interface showing (i) preferential occupation of micropores by BET analysis, (ii) formation and thermal stability of polyhalide species (as detected by Raman spectroscopy and DSC), (iii) charge-transfer mechanism (XPS analysis) and (iv) structural modification by interfacial polyhalide formation (by XRD and SAXS analysis). These carbon-halide nanocomposites deliver improved electrochemical capacity and develop faradaic plateaus around 2.5-3.3 V (vs Li/Li^+). The galvanostatic electrochemical performance as well as cycling stability over 800 cycles will be demonstrated to gauge these materials for electrochemical supercapacitors as well as hybrid capacitors.

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Capacitive Detection of DNA Modification and Hybridization Process Using Tailored Interdigital Microelectrode Arrays

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Interest in miniaturized bio-sensing techniques has grown in the past decades for their application in health care, environmental, military and food industries. DNA and aptamer bioreceptors have gained popularity in biomedical research for fast and easy diagnostic of diseases since each living organism contains a specific DNA sequence that can be selectively identified. Here, we propose a non-faradaic, label-free, electrochemical method based on capacitance measurement to sense DNA surface modification and hybridization. We created custom-made gold interdigital microelectrodes arrays using photolithography technique. Silver electroplating was used to make a stable silver silver/chloride quasi-reference electrode. Self assembled monolayers of B. Anthracis aptamer at two different surface coverage were made and exposed to complementary, non-complementary and mismatch strands to study the hybridization and/or non-hybridization processes by means of double layer capacitance (Cdl) measurements at two given applied potentials using Electrochemical Impedance Spectroscopy (EIS) analysis. An average percentage change in Cdl of 39.0% and 16.3% were obtained for the low and high B. Anthracis aptamer coverage respectively when exposed to its complementary target. The conditions that showed better distinction between strand interactions were low surface coverage at 0.3V applied potential. Overall results shown that double layer capacitance is a measurable property to detect specific DNA sequences.

Mn-Doped ZnO Nanorods Diluted Magnetic Semiconductor for Label-Free Photoelectrochemical Aptasensing

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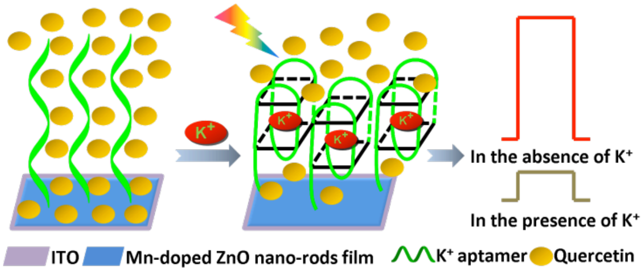
A label-free photoelectrochemical (PEC) aptasensor for K^+ was firstly constructed using Mn-doped ZnO nanorods diluted magnetic semiconductor prepared by a one-step electrodeposition. The fabricated PEC aptasensor was based on the highly specific interaction of K^+ and its aptamer. K^+-stabilized G-quadruplex structure can efficiently prevent the electron donor quercetins from reaching the G-quadruplex-functionalized Mn-doped branched ZnO nanorods photoanode and then proportionately affect the enhanced photocurrent response. The ultrasensitivity of the PEC aptasensor was mainly due to the rapid separation of the more long-lived photon-generated carriers and the expanded visible light absorption caused by Mn doping. Under the optimized experimental conditions, the fabricated biosensor was linear in its response to the concentration of K^+ in the range of 0.012 to 11.901 nmol L^{-1} with a detection limit of 3.781 pmol L^{-1} at a signal-to-noise ratio of 3. The common coexist ions did not interfere with the detection of K^+ in urine sample, and the results corresponded well with those obtained by ICP-MS. This novel fabricated label-free PEC aptasensor exhibited good performance with its ultrasensitivity, good selectivity, simplicity, and economy. This work not only extends the application of diluted magnetic semiconductor, but also paves a new way for label-free PEC aptasensor.



Scheme 1. Schematic illustration of the PEC detection of K^+ by the conformation change of the G-quadruplex aptamer.

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Asymmetric Sodium-ion Supercapacitors with Faradaic Electrodes of Nanostructured Carbons

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Various nanostructured carbon materials have been demonstrated as high power faradaic electrodes, with potential for applications as counter electrodes in asymmetric supercapacitors.[1] These can be expected to exhibit a high power density due to the short transport path for ions and electrons, delivering relatively high capacity via intercalation of ions into the carbon structure. Moreover, pseudocapacitor-like behavior was observed for some of the nanostructured carbon-based faradaic electrodes when storing ions including lithium and sodium, which further increases the power density.[2] One interesting observation is that sodium ions can be stored as fast as lithium ions in the nanostructured carbons, despite the relatively large size of sodium ions; this is likely due to the pseudocapacitive behavior, which is less sensitive to the bulk diffusion of ions.[3] It should be noted that in contrast to lithium intercalation, sodium intercalation into graphitic layers is considered impractical because of the small interlayer space.[4] Considering the similarity to lithium-ion storage in terms of chemistry, and the relative abundance of sodium, it follows that asymmetric sodium-ion supercapacitors using pseudocapacitive nanostructured carbon as a faradaic electrode have potential as a viable alternative to conventional lithium-ion batteries for energy storage.

Here, we report ultra-thin hollow carbons as a faradaic electrode material for asymmetric sodium-ion supercapacitors. The ultra-thin hollow carbons were prepared using a pyropolymer (silk protein) via a template method, followed by carbonization. It can be dissolved and easily reformed into various morphologies resulting from self-assembly.[5] This regenerated silk fibroin in the presence of silica nanospheres can be further transformed into a nanostructured, nitrogen-doped, carbon-based material via a simple pyrolysis process.[6,7] By exploiting the hollow morphology, we aimed to further increase the power by reducing the thickness of the walls of the hollow carbons, as well as by doping them with nitrogen. The ~3 nm thick carbon walls can be expected to lead to rapid sodium ion kinetics, and provide a large mass density of sodium sites in the nanostructured carbon. Furthermore, doping with nitrogen modifies the electronic structure, leading to an increase in the density of electron donor states.[8] This modification of the electronic structure may also be expected to increase the electrical conductivity, increase the wettability in an organic electrolyte, and provide more sites for coordinating sodium ions.

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Electrocatalysis with Polyoxometalates

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Polyoxometalates (POMs) are stable clusters of anions that consist of multiple transition metal oxyanions linked together by shared oxygen atoms to form large, closed 3D frameworks. POMs exhibit a wide range of structural redox and catalytic properties both in the dark and under illumination and can also be used as stabilizers for the formation of nanocatalysts. Consequently, POM-based materials are effective catalysts for a wide variety of reactions including the important water oxidation reaction. Significantly, they are highly stable in a range of redox levels and their thermodynamic and catalytic properties can be tuned by changing the heteroatoms without affecting their gross structures. For all of these reasons, POMs are of substantial fundamental and applied interest. In this lecture, a brief overview of multi-electron transfer studies using a range of voltammetric methods will be given. Advantages and limitations of the various techniques will be considered. Recent findings on the application of a tetra-ruthenium POM for electrocatalytic water, methanol and ethanol oxidation aided by novel aspects of Fourier transformed large amplitude ac voltammetry (FTACV) will then be presented. This highly sophisticated FTACV technique provides new insights into mechanistic aspects of water and alcohol oxidation under POM- based catalytic turnover conditions. The work described in this lecture represents the outcome of ongoing collaboration of the Monash Electrochemistry Group with Prof Craig Hill, Yurii Geletii and their colleagues at Emory University.

Electropolimerization of L- and D- glutamic acids on Glassy Carbon electrodes. Determination of hydrochlorothiazide.

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The modification of electrodes by electropolymerization is a technique widely used for immobilizing monomers on the electrode surface. These electrodes have an easy preparation, good stability, reproducibility, and they show improved selectivity and sensitivity in electroanalytical measurements. Glutamic acid is one of 20 essential amino acids and has a great interest as modifier specie due to its easy immobilization on the electrode surface. The film of poly glutamic acid (PGlA) facilitates the transfer of charge [1].Carbon electrodes modified with PGlA have been used for the determination of different analytes in solution such as drugs and metabolites [2].

Hydrochlorothiazide (HCTZ) (6-chloro-3,4-dihydro-2H-1,2,4-benzo-thiadiazine-7-sulfonamide 1,1dioxide) is a diuretic commonly used in Chile to treat edema, hypertension and diabetes. The analytical identification and quantification of HCTZ by high-performance liquid chromatographic is the metodology more used according to USP 26.

In this work, the modification of glassy carbon electrodes with both, L- and D-glutamic acid monomers was performed for the subsequent determination of HCTZ by differential pulse voltammetry. The modification conditions were: 0.02 M L or D- glutamic acid in 0.04 M hydrochloric acid solution, scanning 15 voltammetric cycles at 100 mV s^{-1}. Figure 1 shows the comparative response of HCTZ on GC and GC/L-PGlA. On both electrodes, HCTZ showed a symmetric and resolutive signal. However using GC/L-PGlA modified electrode (a) the current response increase 1.8 times respect to GC (b). An analytical methodology was developed comparing the results with chromatographic and spectrophotometric techniques.

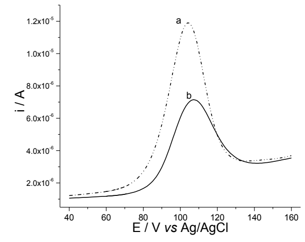

Figure 1: DP voltammograms recorded at (a) GC/L-PGla and (b) bare GC electrodes, in presence of 0,1 M HCTZ in Buffer Britton-Robin solution 0,1 M pH 2.

The comparison between, D and L GC/ PGlA electrodes was performed by AFM studies and evaluating the response of HCTZ on each electrode.

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Electrochemiluminescent Visualization of Singlet Oxygen Induced by Electroactive Zinc Porphyrin Microchip in Aqueous Media

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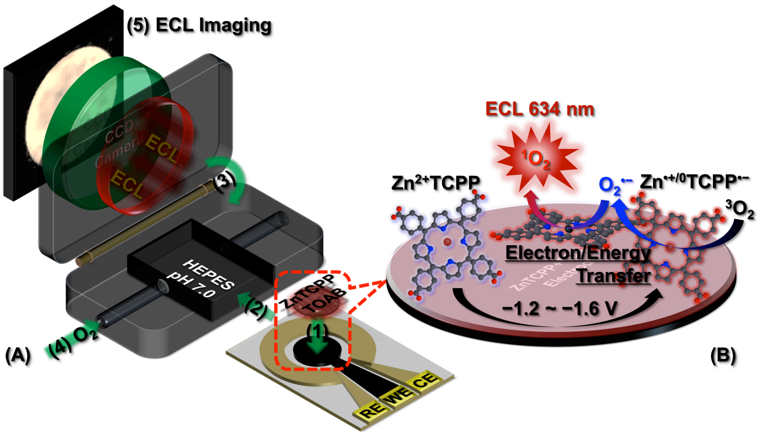
A porphyrin-based electrochemiluminescent (ECL) imaging system was fabricated for monitoring the concentration of singlet oxygen ($^1O_2$) (**Scheme**). Distinct from the ECL inability of numerous organic species in aqueous solutions, a strong and stable red irradiation at 634 nm could be stimulated electrochemically on zinc(II) *meso*-tetra(4-carboxyphenyl) porphine (ZnTCPP)/tetraoctylammonium bromide (TOAB) in the physiological condition. In terms of *in situ* electron paramagnetic resonance and ECL spectroscopies, the nature of ECL was thoroughly investigated, being exactly the chemiluminescence from $^1O_2$ produced during the successive electro-reduction of ZnTCPP. Meanwhile, the excellent film-making capacity of amphiphilic TOAB as a potent ion barrier granted the luminophores a micro-order and patternable electrode modification. Such platform was exceptionally tolerant of pH variation, facilitating a durable solid-state ECL visualization under potentiostatic electrolysis and time exposure in the charge-coupled device (CCD) camera. For flow-injection and real-time detection, a chip-mounted microfluidic cell was customized and manufactured. An extremely sensitive and simple vision-sensing of O_2 was further achieved with a real determination limit as low as nanomolar level and wide linear range over 5 orders of magnitude. The developed ECL imaging system is the first and an eco-friendly case in the cathodic range, thus would supplement the primary anodic imaging library, showing great promise in multiplexed and colorimetric assays as well as oxygen-involved activity studies in future.



Scheme. (A) General principle of the microchip-based ECL visualization, and **(B)** Schematic mechanisms for ECL of $^1O_2$ at TOAB/ZnTCPP/SPE.

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Photocatalytical Synthesis of Prussian Blue Functionlized TiO_2 Nanotube Arrays: an Amperometric Sensing Platform for Glucose Detection

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Prussian blue (PB), formula $Fe_4^{III}[Fe^{II}(CN)_6]_3$, owing to the high activity and selectivity toward the reduction of H_2O_2 and O_2, has been employed extensively as an ''artificial enzyme peroxidase'' in the construction of electrochemical amperometric biosensors. Up to now, many methods have been used to prepare PB-modified electrodes. Recently, we have demonstrated that PB could be decorated on semiconductor surfaces via photocatalytical deposition or galvanic displacement from a ferricyanide and ferric ions containing solution. Such nanoscaled interfaces between semiconductor and PB are considered to be important for applications of semiconductor, such asoptoelectronics, clinical diagnosis, ion-selective properties, battery applications, and microelectro-mechanical systems. Based on the photocatalytic property and their unique architectural morphology, anodically grown TiO_2 nanotube arrays (TiNTs) can be a promising supporting electrode material in construction of electrochemical biosensors because the anodic TiNTs are grown directly on a titanium-metal substrate. In this context, we construct an enzymatic biosensor based on TiNTs as a supporting electrode on which PB and enzyme glucose oxidase (GOx) have been immobilized. For this, PB nanocrystals are deposited onto the nanotube wall photocatalytically using the intrinsic photocatalytical property of TiO_2. The tube wall is subsequently modified with a layer of polymeric matrix of poly-(1,2-diaminobenzene) (poly(1,2-DAB) by electrochemical polymerization to integrate PB and GOx into the nanotubes, which on the other hand also avoids the leaching of PB. Due to the synergistic effect of the good electrical conductivity of AuNPs and the high electrocatalytic ability of PB, the resulting electrode exhibits a fast response, wide linear range, and good stability for glucose sensing. The sensitivity of the sensor is as high as 248 mA M^{-1} cm^{-2}, and the detection limit is about 3.2 μM. These findings demonstrate a promising strategy to integrate enzymes and TiNTs, which could provide an analytical access to a large group of enzymes for bioelectrochemical applications including biosensors and biofuel cells.

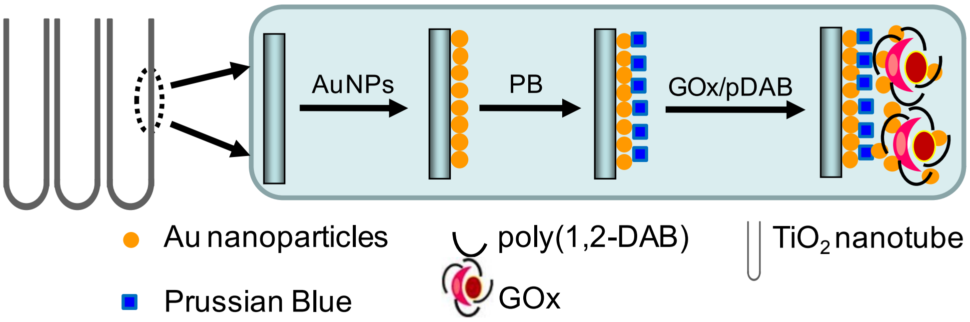

Figure 1. Schematic illustration for the preparing of PB/GOD "bienzyme" decorated electrode on TiO_2 nanotube arrays.

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Synthesis and electrochemical properties of LiFePO4/C/GO composite cathode material prepared by hydrothermal method

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Abstract

The LiFePO4/GO (LFP/Graphene Oxide) composite cathode material was synthesized by hydrothermal process. A suitable amount of Graphene Oxide was added into the LFP mixing precursors in the hydrothermal process. The ascorbic acid was also added to prevent Fe^{2+} oxidation during the processing. The pH was controlled at 6.5. The hydrothermal process was conducted at 180oC for 8 h. After hydrothermal treatment, the LFP precursor mix 10 wt.% Polystyrene by ball milling methode . The LFP/C/GO precursor was further sintered at 650^{o}C for 7 h in 95%Ar-5%H_2 atmosphere. The properties of the as-prepared LFP/C cathode materials were examined by XRD, SEM/EDX, TEM, micro-Raman spectroscopy, EA, and XRF. The 2032 coin half-cell was assembled to examine the electrochemical performance of the LFP/C cathode materials. The galvanostatic charge-discharge test was conducted in the potential range of 2-3.8 V using LiPF6 + EC: DEC (1:1, v/v) electrolyte at various C-rates (0.1C-10C). It was found that the residuals carbon content is around 3.65%. The carbon layer thickness on the LFP/GO/C material is around 4-5 nm. It was revealed that the discharge capacities of the LFP/C cathode materials are 149, 145, 131, and 95 mAh g-1, respectively, at 0.1C, 0.2C, 1C and 10C discharge rate.

Keywords: LiFePO4/GO/C, Hydrothermal, Polystyrene, Graphene Oxide

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Study of electrochemical performance of $LiFe_{0.5}Mn_{0.5}PO_4$/C composite cathode doped with yttrium and chloride

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Abstract

This study reported a simple solid-state method to prepare $LiFe_{0.5}Mn_{0.5}PO_4$/C (denoted as LFMP/C) composite materials by using LiH_2PO_4、MnO_3、$FeC_2O_4 . 2H_2O$、citric acid ($C_6H_8O_7$)、sucrose ($C_{12}H_{22}O_{11}$)、$Y(NO_3)_3$ and NH_4Cl. The citric acid was used as a complex agent and sucrose was used as a carbon source. $LiFe_{0.495}Mn_{0.495}Y_{0.01}PO_4$/C (denoted as Y-doped LFMP/C) and $LiFe_{0.5}Mn_{0.5}Cl_{0.03}PO_{3.97}$/C (denoted as Cl-doped LFMP/C) was synthesized by a solid-state method. The composite materials was sintered at 650°C in an Ar atmosphere for 15 h. The characteristic properties of as-synthesized LFMP/C composite cathode materials were examined by micro-Raman spectroscopy, XRD, SEM/EDX, TEM, EA and XRF. The 2032 coin half-cell was used to investigate the electrochemical performance at various rates. It was found that the specific discharge capacities of $LiFe_{0.495}Mn_{0.495}Y_{0.01}PO_4$/C composite cathode materials can achieve around 129.18 and 106.77 mAh g^{-1}, respectively, at 0.1 and 1C rate. It was found that the discharge capacities of $LiFe_{0.5}Mn_{0.5}Cl_{0.03}PO_{3.97}$/C composite cathode materials are around 158.49mAh g^{-1} and 141.99mAh g^{-1}, respectively, at 0.1 C and 1C rates. Apparently, it was found that the as-synthesized Cl-doped LFMP composite materials show good promising candidates for high energy Li-ion battery applications.

Keywords: $LiFe_{0.5}Mn_{0.5}PO_4$, chloride-doping, yttrium-doping, Cathode materials

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High electrochemical performance of surface-modified $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ cathode materials

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Abstract

This work reported a simple solid-state method to prepare $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ composite materials by using LiOH、MnO_2、$Ni(OH)_2$、D-Tartaric Acid. The D -Tartaric Acid was used as a complex agent. The $Li_{0.75}La_{0.42}TiO_3$ (LLTO) was used to surface modify $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ by a sol-gel method. The characteristic properties were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), TEM, micro-Raman spectroscopy, the AC impedance method, and galvanostatic charge-discharge method. The 2032 coin half-cell was used to examine the electrochemical performance at various rates. It was found that the $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ cathode material with 1wt.%LLTO oxide shows the best performance. The discharge capacity of the 1wt.%LLTO-coated $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ cathode material is around 238.54 mAh g^{-1} at 0.1C rate; 187.61mAh g^{-1} at 1C rate. In addition, the long-term cycling performance for surface-modified Li-rich oxide composite was conducted at 0.1C rate for 30 cycles and 1C rates for 100 cycles; it was found that the decay rates of 0.1C and 1C rates are 0.461%/cycle and 0.179%/cycle, respectively. It was revealed that LLTO-coated $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$ composite cathode material showed a promising candidate for Li-ion battery application.

Keywords: $Li_{1.2}Ni_{0.16}Mn_{0.56}Co_{0.08}O_2$, composite cathode material, Solid-state method, D-Tartaric acid, Li ion battery, $Li_{0.75}La_{0.42}TiO_3$ (LLTO)

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Ionic Liquid-Assisted Electron Transfer in Micelles for Simultaneous Electrodeposition of Uniform Ag Nanoparticles at Electrode Surface and in Bulk Microemulsions

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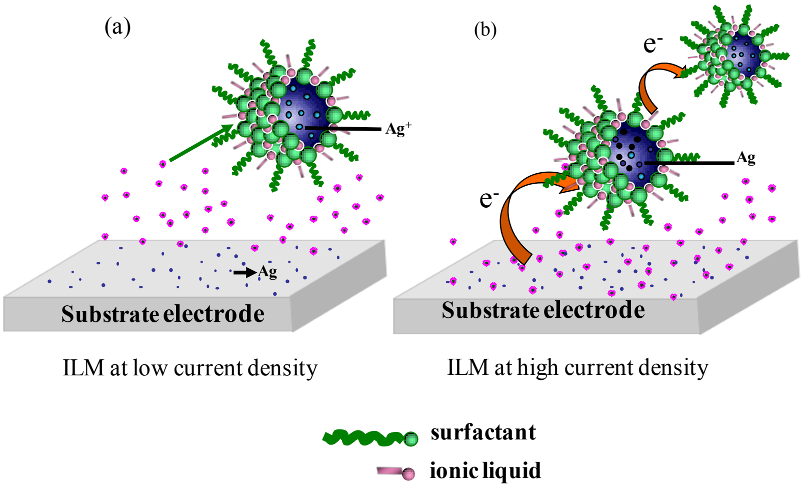
The synthesis of metal nanoparticles with controllable size from aqueous or organic solutions has long been a scientific and technological challenge. In this paper, we show an unique electrodeposition approach from ionic liquid microemulsions (ILM) which enables simultaneous fabrication of uniform controllable Ag nanoparticles at both electrode surface and in bulk solution. In the ILM system containing cetyltrimethylammonium bromide (CTAB), butanol, 1-butyl-3-methyl- -imidazolium chloride ([BMIM]Cl) and an aqueous solution of silver nitrate, uniform Ag nanoparticles with a narrow size distribution of 20 ~ 50 nm could be electrodeposited on the cathode surface at low deposition current (0.2 ~ 1.5 mA·cm^{-2}). The size and size distribution of Ag nanoparticles can be adjusted by tuning the deposition current, time, temperature and IL concentrations. Remarkably, at high deposition current (> 1.5 mA·cm^{-2}) the electrodeposition of Ag nanoparticles takes place not only on the electrode surface but also beyond into the bulk microemulsion phase. Uniform Ag nanoparticles of diameters 2 ~ 13 nm thus can be obtained from the bulk ILMs. It is found that the ionic liquid plays a quaternary role as a soft template and co-surfactant for the formation of micro-reactors, an electrolyte for enhancing conductivity, and an electron carrier facilitating electron transport between nanodroplets for Ag reduction. The electrocatalytic activity of the electrodeposited Ag nanoparticles has been investigated for oxidation of glycerol for potential applications in direct alcohol fuel cells.



ILM at low current density

ILM at high current density

Fig.1. Schematic diagram of electrochemical synthesis of Ag nanoparticles from the ILM at (a) low deposition current density, and (b) high deposition current density.

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Substantial Improvement of Chemical Production from Bio catalyzed Polymer Electrode in Bioelectrochemical System.

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Utilization of carbon dioxide and production of multi-carbon chemical compounds are one of the recent developments in bioelectrochemial system (BES). In Bioelectrochemial system (BES) microbes utilized the carbon dioxide as a carbon source and electron from externally polarized cathode for the synthesis chemical commodities (Lovley et al 2012). This technology mainly depend on the performance of the electro autotrophic bacteria, cathode material and reactor configuration for the enhancement of electron exchange rate (Lovley et al 2012). The approach of modification of cathode materials are important aspectsto increase the production rate and making this technology robust and economically worthwhile (Giddings et al 2015). The surface modification of cathode improves the chemical production rate through the improvement of electron transfer rate at microorganism- electrode interface. Principally, the enhanced electrode surface influences on the adherence of the bacterial cells, formation of biofilm, and transformation of the electron from the electrode to bacterial cell (Gao et al, 2015). Recently, PEDOT: PSS conductive polymer has been investigated and employed as novel anode materials in the microbial fuel cell. It is one of the premising electrode materials for MES system due to its low manufacturing cost, high electrical conductivity, and good transparency, possesses a better stability of conductivity which optimized the energy production rate in microbial fuel cell. (Wang et al 2013) In this study, Carbon cloth was polymerized with PEDOT: PSS and carbon dioxide was used as carbon source for the production of acetate in MES system. The production rate was improved three times compare to unmodified electrode. To the best of our knowledge, this study first time reported the application of PEDOT electrode and enhancement of acetate production rate, current density in microbial electrosynthesis by using *sporomusa ovata*.

Keywords: - Microbial electrosythesis, CO_2 reduction, Polymer, sporomusa ovata

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Surface Modification of $LiMn_2O_4$ for Enhanced Performance at Elevated Temperature

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$LiMn_2O_4$ is widely used as cathode material for lithium ion batteries, however, it suffers from the drawback of poor cycling stability, which is mainly associated with manganese dissolution during battery operation, especially at elevated temperatures. To overcome these problems, we have developed several new coating technologies with good uniformity and controllability. The samples with surface modification have been put on cycling and aging tests at elevated temperature and showed improved electrochemical performance.

For example, bronze type TiO_2 coated $LiMn_2O_4$ has been successfully synthesized via liquid phase method combined with electrostatic adsorption. The coating structures were well tuned by adjusting the coating content and heat treatment time. The electrochemical test results showed that 3 wt. % coated cathode exhibits the best cyclic performance with a capacity retention rate of 73.7% after 100 cycles at high temperature. The coating layer 3D pores provide channels for lithium ion transport thus enhancing the rate performance of $LiMn_2O_4$.

The aging experiments were carried out on the surface modified $LiMn_2O_4$. The structure and electrochemical performance after aging experiments are tested to determine the modification mechanism. The results showed that surface modification can effectively improve the stability of the material, reduce the side reaction and reduce cracking as a result of stress accumulation. Besides, the surface coating could also prevent the deposition of $Li_xF_yPO_z$, LiF or other electrolyte component.

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Green synthesis of a biodegradable and conducting material for biomedical applications

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Polylactides (PLAs) have attracted much research attention as biodegradable and biocompatible materials with a vast scope of applications [1] On the other hand, conducting polymers (CPs) such as polypyrrole (PPy), polyaniline (PANi) and polythiophene (PT) have been investigated as electroactive substrates for the culture of especially electrically excitable cells. They have been proved to play an important role in stimulating proliferation, adhesion or differentiation of various cell types.[2] Some approaches which prepare blends of conducting polymers with biodegradable materials, especially with the use of PPy and PANi,[3] have been reported in the literature, but after degradation of the blend, a small amount of these materials remain in the body and can cause some *in vivo* toxicity troubles. To overcome this problems, it was developed a copolymer based on poly(3,4-ethylenedioxythiophene) (PEDOT) covalently linked to poly(L-lactic acid) (PLLA) with conducting and biodegradable properties.

In the present work, the study of the electrochemical behavior of the copolymer PEDOT-*co*-PLLA prepared by chemical synthesis, is presented. Films were prepared by casting and submitted to biodegradation tests using *Proteinase K* as model enzyme, monitoring the weight loss and pH changes in media (biodegradation of PLLA generates ascorbic acid). Also, cell growth assay using PEDOT-*co*-PLLA 1:50 as scaffold for fibroblast cells were performed, investigating the effect of electrical stimulus in the process of proliferation of these cells.

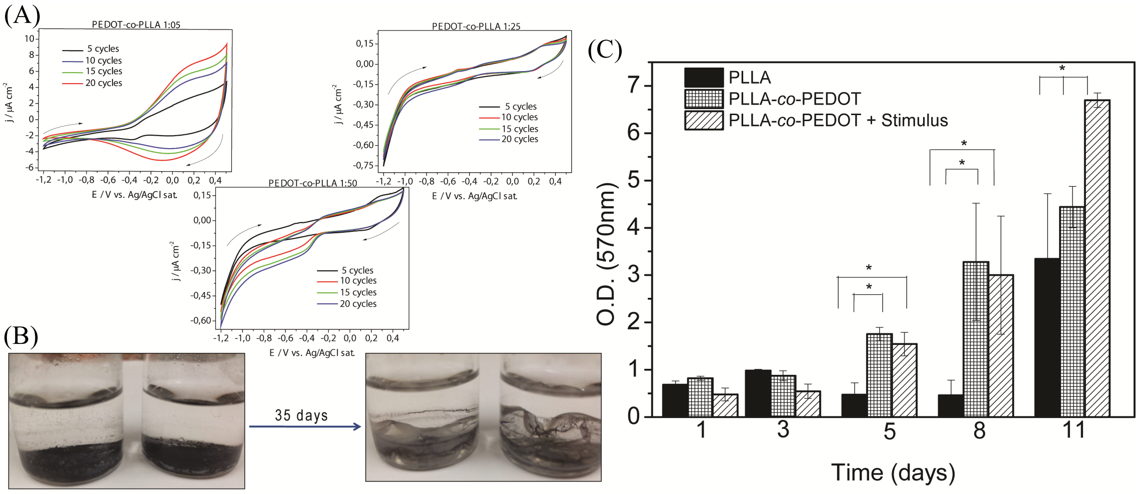

Figure 1 – (A) Cyclic voltammetry of PEDOT-*co*-PLLA 1:05, 1:25 and 1:50, respectively; (B) photography of physical aspects of the polymeric films submitted to biodegradation test after 35 days in presence of *Proteinase K* in PBS and (C) cell growth assay with fibroblast cells.

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Understanding of Improved Electro-catalytic Activity of MoS_2 Nanosheets Synthesized by Liquid Phase Exfoliation

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Recently, MoS_2 nanosheets synthesized by liquid phase exfoliation exhibited the improved electro-activity[1], compared with other synthesis methods (e.g., chemical vapor deposition and chemical exfoliation methods) or its bulk counterpart. Because fundamental properties of materials are determined by the composition, atomic arrangement, and dimensionality, in this case possible reasons mainly include the increasing number of exposed active sites on the edges out of plane, the formation of a hybrid superlattice of alternating inorganic MoS_2 monolayers and organic molecules by intercalation, and the presence of new surface function groups. In this study, we investigated which factor would lead to the improved electro-activity by combining first-principles calculations and electrochemical measurements before and after exfoliation or intercalation. In addition, the as-obtained MoS_2 nanosheets were used to construct electrochemical sensors for detecting heavy metal ions in aqueous solution such as Cu^{2+} and Pb^{2+}.

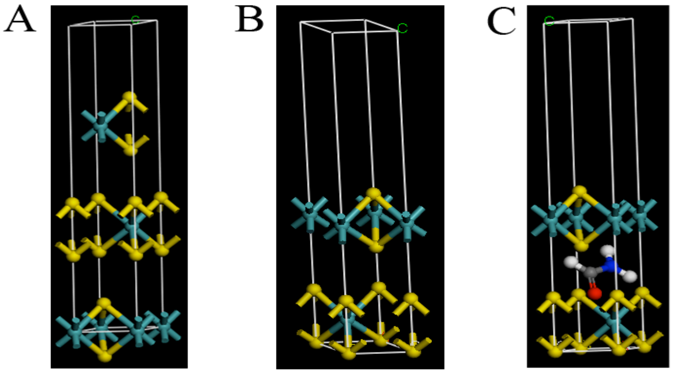

Figure 1. Three-dimensional (3D) cell representation of the crystal structures of bulk MoS2 (A), bilayer MoS_2 (B), and one unit of hybrid superlattice composed of MoS_2 and formamide (C) studied in the present work.

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Voltammetric study of poli-nitrocompounds encapsulated in MWCNT electrode.

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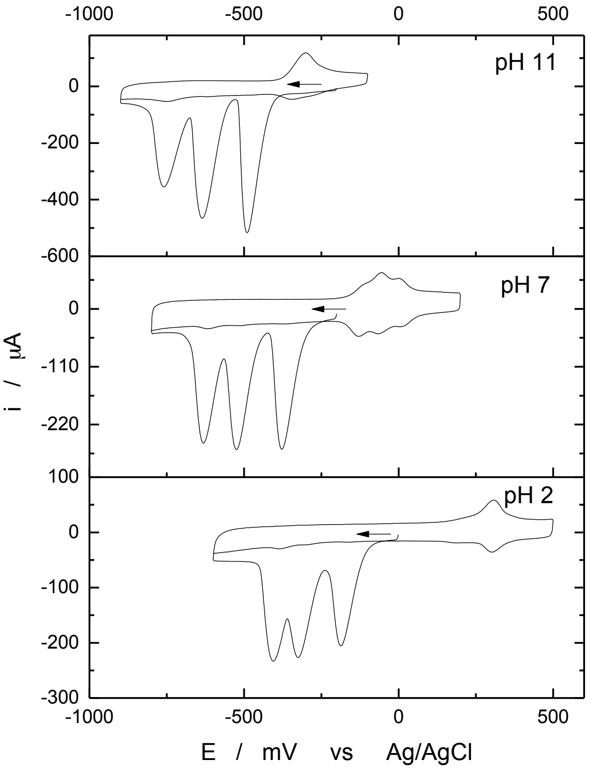
Recently we revealed a new strategy to study the voltammetric behavior of nitrocompounds encapsulated on multi walled carbon nanotubes (MWCNT) or more precisely by being trapped within the pockets of the MWCNTs three dimensional array, without formation of covalent bonding [1]. The procedure involves the encapsulation of nitrocompounds in glassy carbon electrodes (GCE) modified with MWCNT simply by dipping the GC-MWCNT electrode in a solution containing the nitrocompound. We studied different nitrocompounds changing the number of nitro group in the molecule, such as, nitrobenzene, 1,3-dinitrobenzene and 1,3,5-trinitrobenzene. All the nitrocompounds are fairly insoluble in aqueous medium and so are difficult to study in an aqueous medium.

Considering the above property of nitroaromatics is possible to design strategies involving the trapping of the nitrocompound with its subsequent reduction via the 4-electron reduction of the nitro group to the hydroxylamine derivative according to:



$ArNO_2 + 4H^+ + 4e^- \rightarrow ArNHOH + H_2O$ (1)

All nitrocompounds were studied in both GCE and the modified electrode at different pHs in buffer Britton- Robinson. In the first case the electroactive nitrocompound species was in the solution phase but in the second case the species was entrapped in the electrodic 3D phase.

The electrochemistry response was markedly different when the nitrocompound was encapsulated in the MWCNT array. The use of this new strategy based on trapped the nitrocompound in the MWCNT array allows a considerable increase in sensitivity and selectivity of the voltammetric response. We observed an increasing of cathodic current and more selectivity of analytical signals. In the figure we show cyclic voltammograms of 2 mM 1,3,5-dinitrobenzoic acid at pH, 2, 7 and 11 in Britton – Robinson buffer. The following analytical parameters were obtained from a calibration curve for 1,3,5-trinitrobenzene. LOD = 6.7 µM and LOQ = 22.3 µM

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Keywords: nitrocompounds, multiwalled carbon nanotubes, voltammetry.

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Microbial Surface Displaying Enzymes Based Electrochemical Biosensing

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The recent progress in biotechnology provides powerful strategy in exploring analytical applications. In this talk, the construction of whole-cell biocatalysts by expressing of a series of enzymes including xylose dehydrogenase, glucose oxidase, glucose dehydrogenase and organophosphorus hydrolase on cell surface will be highlighted. The enzyme-displayed bacterial cell can not only be used directly without further enzyme extraction and purification, but also it improves the stability of the enzyme. The whole-cell biocatalysts based modified electrodes for sensitive and selective electrochemical biosensors for monosaccharides or organophosphates, *etc* are presented. Therefore, microbial surface displaying enzymes can be engineered to serve as novel electrochemical interfaces, which could be more efficient and cost-effective in comparison with commercial enzymes.

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Aptamer-Initiated On-Particle Template-Independent Enzymatic Polymerization (aptamer-OTEP) for Electrochemical Analysis of Tumor Biomarkers

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Coupled with the ability of fast and quantitative response, electrochemical aptasensors (E-aptasensors) have great potential in the application of early diagnosis of cancer biomarker. In order to determine the rare biomarkers in the complicate clinical samples, scientists are making unremitting efforts towards improving the sensitivity and selectivity of E-aptasensor. Herein, two signal amplification strategies for E-aptasensors are developed for analysis of cancer biomarker carcino-embryonic antigen (CEA). Two DNA aptamers are employed: one of which is thiolated at 3′-terminal and immobilized onto the gold electrode as a capture probe, while the other one is served as signal probe. The two aptamers could “sandwich” the target and signal probe is subjected to the terminal deoxynucleotidyl transferase (TdT)-catalyzed incorporation of biotin labeled dNTPs. Thus the as-generated long DNA oligo tails allow specific binding of numerous avidin modified horseradish peroxidase (Av-HRP), leading to enhanced electrochemical signals. This signal amplification strategy is termed as aptamer-initiated template-independent enzymatic polymerization (aptamer-TEP). To further enhance the signal amplification efficiency, a nanoporbe is fabricated by modification of the signal probes onto the gold nanoparticles (AuNPs). After the formation of the “sandwich” structure, the free 3′-terminals of signal probes on the nanoprobe are catalyzed by TdT to generate hundreds of long ssDNA tentacles, resulting in tens of thousands of HRP catalyzed reduction of hydrogen peroxide and sharply increasing electrochemical signals. This strategy, termed as aptamer-initiated on-particle template-independent enzymatic polymerization (aptamer-OTEP), lowers the detection limit by two orders of magnitude, indicating the outstanding amplification efficiency.

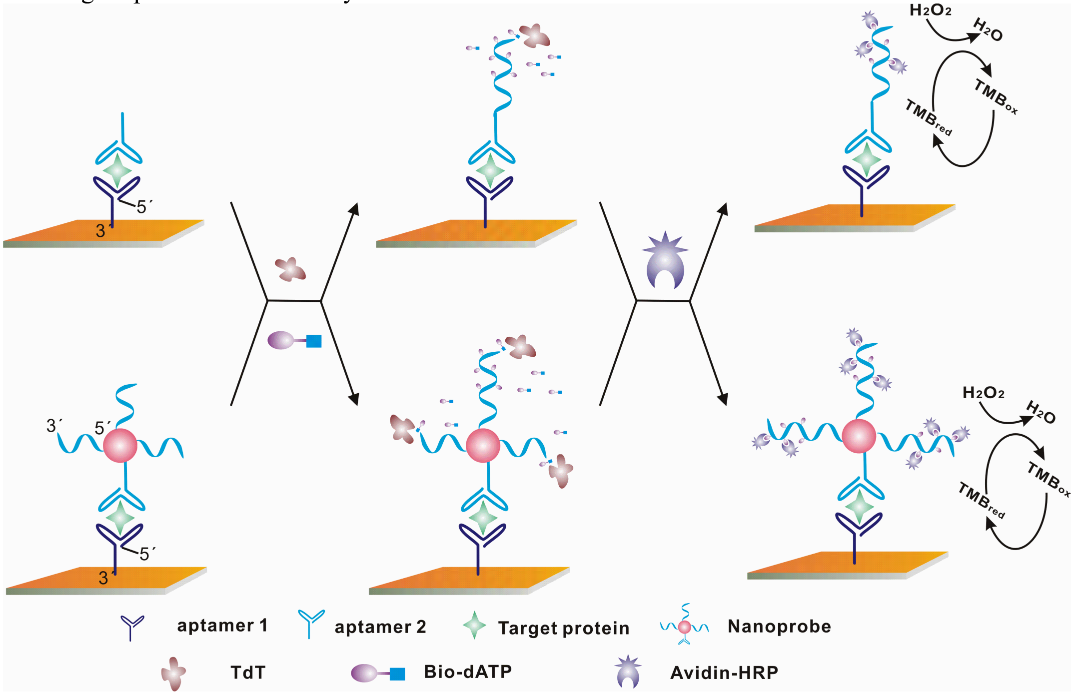

Figure 1. Strategy of aptamer-TEP (upper) and aptamer-OTEP (lower).

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Surface Modified $LiNi_{0.5}Mn_{1.5}O_4$ by Li_2O-$2B_2O_3$ for Lithium-ion Batteries

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Abstract

A Li_2O-$2B_2O_3$ coated $LiNi_{0.5}Mn_{1.5}O_4$ cathode active material was synthesised to enhance the thermal stability of $LiNi_{0.5}Mn_{1.5}O_4$ electrodes used in lithium ion batteries. The Li_2O-$2B_2O_3$ coating prevented the surface of the $LiNi_{0.5}Mn_{1.5}O_4$ electrode from being directly exposed to the liquid electrolyte, thereby suppressing the dissolution of Mn from the electrode surface into the electrolyte and the undesirable formation of a solid-electrolyte-interphase layer. The surface-coated electrode showed 81% capacity retention during high-temperature (60 °C) cycling. The results of the electrochemical impedance spectroscopy (EIS) indicated that the improved performance of the surface-coated electrode slowed the increase in cell impedance during cycling. The Li_2O-$2B_2O_3$ coating effectively slowed the surface of the $LiNi_{0.5}Mn_{1.5}O_4$ electrode from being directly exposed to the liquid electrolyte, thereby suppressing the dissolution of Mn^{3+} ions from the surface of the spinel cathode active material into the electrolyte. The Li^2O-$2B_2O_3$ coating will pave the way for improving the electrochemical cycling of various cathode active materials at elevated temperatures

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Unzipped carbon nanotubes via KOH activation for high specific surface area and trimodal pore structure

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Abstract

We prepared unzipped CNTs with high specific surface area (1123 m^2 g^{-1}) and a trimodal (micro-meso-macro) pore structure through alkali activation. After severe alkali activation (in our study, CNT (C)/KOH = 1:10 (w/w) at 1000 °C), various pores were initially formed on the surface. Subsequently, a longitudinally unzipped structure was obtained as the individual pores connected. In contrast with other methods to prepare unzipped and porous CNTs, this method is economical and scalable because it enables a one-step synthesis of unzipped and porous CNTs. As per the non-localized density functional theory (NL-DFT), the distribution of micro-meso pores showed evidence of unzipping because the peak for pore sizes <1 nm, measured from the partially opened tips of the pristine CNTs, was broadened. Since the tips were perfectly opened after activation, this means that the micropores on the unzipped structure increased. In addition, the results showed that the unzipped porous CNTs had a trimodal pore structure. This structure resulted in increased specific surface area, as well as energy storage and adsorption capacities. The maximum energy density of the unzipped porous CNTs in ultracapacitors based on an organic electrolyte was 50 W h kg^{-1}. Thus, the method is suitable for fabrication of unzipped porous CNTs, which show potential as energy efficient materials.

Modified Electrodes Based on Non-Traditional Electrode Materials

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The presentation will be focused on the application of modified electrodes for detection of submicromolar concentrations of biologically active organic compounds important from the point of view of the protection of environment and human health. Attention will be paid to chemical/biochemical modification of amalgam electrodes [1-3] which can serve as non-toxic substitute of mercury electrodes with similar potential window, of screen printed carbon electrodes [4], of carbon film electrodes [5] and of boron doped diamond film electrodes [6] with probably the broadest available potential window and lowest noise of all available electrode materials. Modification with surface active substances, various nanoparticles, enzymes [3], DNA [7] and other modifiers will be discussed. The application of this approach for detection of environmental carcinogens, tumor biomarkers and biomarkers of exposition both in batch (differential pulse voltammetry, square wave voltammetry, adsorptive stripping voltammetry) and in flowing systems (FIA or HPLC combined with amperometric detection) [8] will be demonstrated.

Acknowledgement
This work was financially supported by the Grant Agency of the Czech Republic (project P206/12/G151).

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Electrochemical Sensing Based on Modified Interfaces and Analytical Instrument-Integrated Applications

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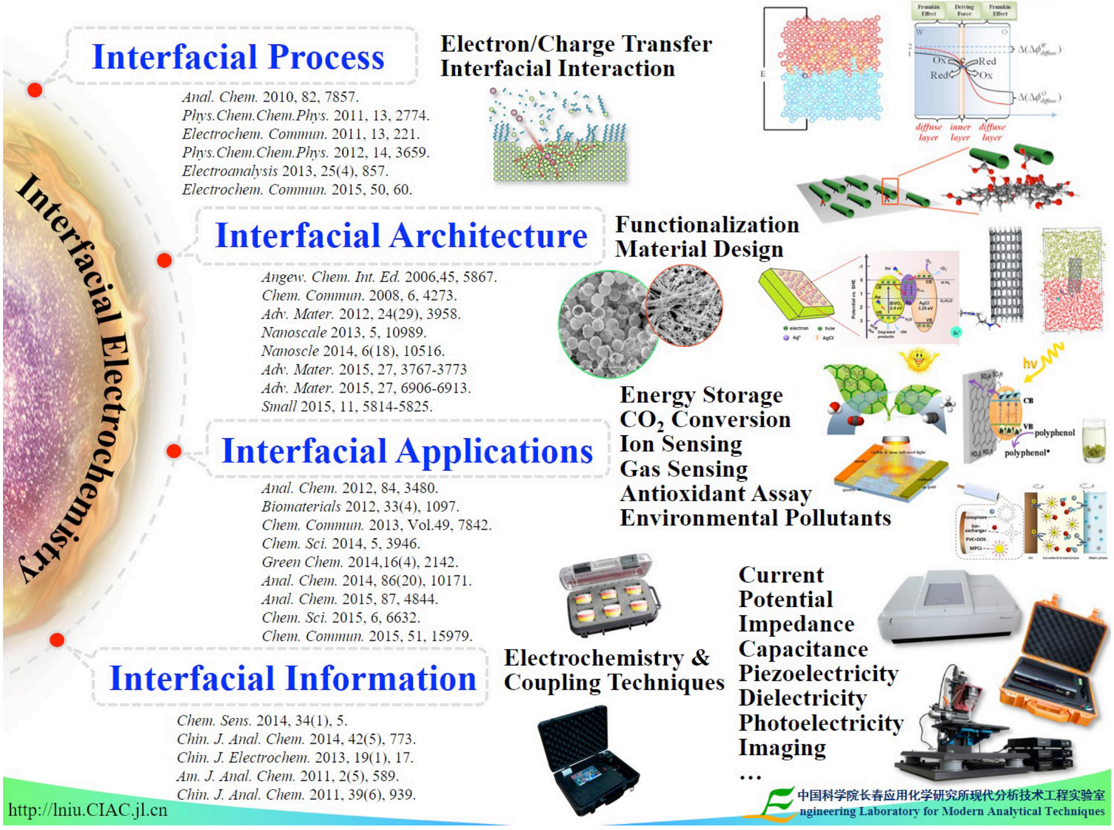
Fundamental electrochemical investigations in combination whatever with materials, environment, life science, and other disciplines, only those 3 possible & practical applications for the human being are available at moment, such as new methods, devices and instruments.

As known, electrochemistry technique is an important member in the whole family of the instrumental analysis. Especially, in coupling with other techniques, we can know much information about the interfacial interaction, structural features, reaction process, mass transfer, etc. during electrochemical running. Unfortunately, imported instruments & equipment occupies the leading position in China within the past decades, electrochemistry system is also still the world of imported products in China, such as Princeton, CHI, BAS, Gamry, Biologic, etc. Besides those electrochemical instruments, some typical and daily-used electrochemical sensors, such as blood glucose analysis, industrial control gas sensors, heavy metal ion monitoring, blood gas analysis, met the same problem in China.

With great increase of human industrial production, water quality analysis is becoming more and more necessary. A few typical electrochemical devices and methods for water monitoring, such as DO, COD, heavy metals, etc. have been developed successfully. In addition, various methods and sensors for bioanalysis & food analysis have been explored too.

Furthermore, series of electrochemical instruments have been completed, which ranged from basic model to advanced, from potentiostat to bipotentiostat, even to multichannel, from integrated spectrometers to electrochemical imaging & etching components, etc. Those developed instruments have been widely used in many institutes & universities in China.



Interfacial Process

Electron/Charge Transfer
Interfacial Interaction

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Interfacial Architecture

Functionalization
Material Design

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Interfacial Applications

Energy Storage
CO_2 Conversion
Ion Sensing
Gas Sensing
Antioxidant Assay
Environmental Pollutants

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Interfacial Information

Electrochemistry &
Coupling Techniques

Current
Potential
Impedance
Capacitance
Piezoelectricity
Dielectricity
Photoelectricity
Imaging
…

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Using the Electrochemistry of Phenylenediamines as a Measure of the Hydrogen Bonding Abilities of Alcohols in Organic Solvents

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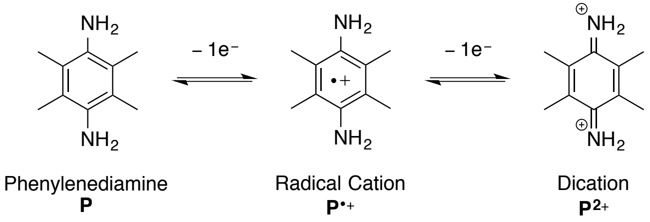
In organic solvents, tetramethylphenylenediamine (P) is able to be electrochemically oxidized in two chemically reversible one-electron oxidation processes (Scheme 1) to form first the radical cation ($P^{\bullet+}$), followed by further oxidation to the quinonediimine dication (P^{2+}). The potentials at which these oxidation reactions occur are sensitive to the presence of hydrogen bond donors and acceptors, and thus vary accordingly to their amount present.

Scheme 1. Oxidation of tetramethylphenylenediamine in acetonitrile.



Because of weak hydrogen bonding between the nitrogen atom of P and ethanol (EtOH), the potential of the $P/P^{\bullet+}$ redox couple ($E_{P/P\bullet+}$) remains unchanged with increasing concentrations of the alcohol (Figure 1a). However, the potential of the $P^{\bullet+}/P^{2+}$ redox couple ($E_{P\bullet+/P2+}$) shifted to less positive values because of stronger hydrogen bonding interactions between the ethoxy oxygen atom and hydrogen atom of P^{2+}. A different trend is observed when trifluoroethanol (TFE) is used (Figure 1b). The stronger interaction between the nitrogen atom of P and the alkoxy hydrogen atom shifts $E_{P/P\bullet+}$ towards more positive potentials with increasing alcoholic content, while $E_{P\bullet+/P2+}$ is unaffected since the interaction between the alkoxy oxygen atom and the hydrogen atom of P^{2+} is rather weak.

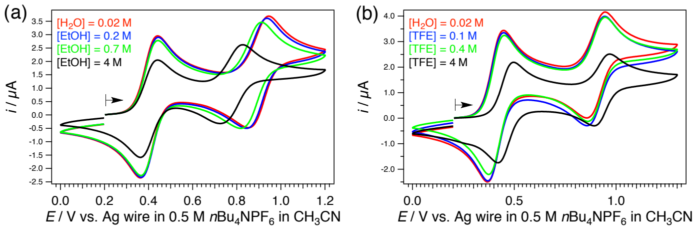


Figure 1. Cyclic voltammograms of 1.0 mM P at different concentrations of (a) EtOH and (b) TFE in the presence of 0.1 $n\mathrm{Bu_4NPF_6}$ and recorded at a scan rate of 0.1 V s^{-1} at 25 ± 2 °C with a 1 mm diameter planar glassy carbon electrode. The initial voltammograms obtained before the addition of alcohols are indicated in red solid lines with their measured trace moisture content.

This work will illustrate the versatility of P for qualitative measurements of the hydrogen bonding abilities of alcohols in solution through the electrochemical parameter $\Delta E = |E_{P/P\bullet+} - E_{P\bullet+/P2+}|$, which decreases as the concentration of alcohol increases. ΔE accurately reflects the strength of the hydrogen bonding interactions because the effects of uncompensated solution resistance and heterogeneous electron-transfer rates are cancelled. Furthermore, other competing interactions such as ion pairing with the supporting electrolyte and interactions with trace water and the solvent are considered. The resulting plots of ΔE against the concentrations of different alcohols are highly reproducible and can be used to distinguish primary, secondary and tertiary alcohols and even diols.

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Tetrathiafulvalene as a film forming additive for high-voltage lithium ion positive electrode

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For the last decades, lithium-ion batteries (LIBs) have been used as the power source for mobile electronic devices [1]. In the near future, the market of LIBs seems to expand to the power sources for electric vehicles and energy storage devices [2]. The existing LIB technologies, however, have serious performance limitation on aspect of energy density as well as safety and cycle life for their new applications. As an effort to increase the energy density of LIBs, a few high-voltage positive electrodes have been tested [3]. One of the spotlighted materials is the lithium-excess layered oxides (also named over-lithiated layered oxides, OLOs), $Li_xMn_yCo_zNi_aO_2$, which have a higher working voltage [4-5]. The high working voltage must be beneficial for the energy density of LIBs, but poses a serious problem on the electrolyte stability against oxidation. One way to solve or mitigate this problem must be an addition of film-forming agents into electrolyte solution, which decompose to form a protective layer on OLO surface to prevent further electrolyte decomposition [6-9].

In this study, we found that cathode surface modification using tetrathiafulvalene exerted a significant influence on battery performance. To test the feasibility for a film-forming agent, their oxidation potentials are calculated by using the density functional theory (DFT) and compared with those of the carbonate solvents. Superior cycle performance indicated that stable films could be formed on the cathode surface by using these additives.

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Non-flammable Binary Electrolytes for LIBs from Pyrrolinium-based Ionic Liquid and Carbonate

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Lithium-ion batteries (LIBs) would be one of the most important energy conversion/storage systems owing to their advantages such as a high energy density, negligible memory effect and less self-discharge. However, the poor thermal stability of commercial carbonate electrolytes in LIBs is a main obstacle to extend their applications to electric vehicles (EVs) or energy storage systems (ESSs). To overcome its critical limitation, alternative electrolytes that have a good thermal stability with a wide electrochemical window have been intensively explored allowing the LIBs to be more applicable. In this respect, ionic liquids (ILs) have been considered as an attractive electrolyte candidate because of their stable thermal behaviors. ILs exist liquid at room temperature even if they are composed of cations and anions, and show unique electrochemical, thermal, and physicochemical properties. In contrast, their practical applications as electrolytes for LIBs have been limited because of its poor electrochemical performance. Previously reported imidazolium-based ILs with high ionic conductivity and low viscosity have some disadvantages such as the narrow cathodic polarization, which was attributed to an reactive proton at the C-2 position of the imidazolium ring. Pyrrolidinium- or piperidinium-based ILs with a saturated cyclic structure exhibited more stable electrochemical stability than the imidazolium-based ILs, but their lower ionic conductivity and high viscosity should be improved for the practical application as thermally stable electrolytes of LIBs.

In the present study, we will present some binary electrolytes composed of novel pyrrolinium-based IL with commercial carbonate. The pyrrolinium-based IL was designed to have some task-specific functionalities such as a planar double bond, an ether linkage for efficient Li^+-binding, and no reactive C-H bond. We expected that a mixture of non-flammable pyrrolinium-based ILs and conventional carbonate would exhibit the synergic effects to overcome the aforementioned issues. First of all, the flammability of the carbonate solvent can be suppressed by blending the non-flammable ILs with the commercial carbonate electrolyte. Secondly, the conventional carbonate electrolyte with high ionic conductivity and low viscosity could improve the relatively poor physicochemical properties of the ILs. We will also present the physicochemical, thermal, and electrochemical properties of several pyrrolinium-based binary electrolytes and the electrochemical performance of the binary electrolytes to be applicable as electrolytes of LIBs.[1]

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Electrochemical Performances of $Li_3V_2(PO_4)_3$ Cathode Materials for Li-Ion Battery

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Lithium ion batteries (LIBs) have been used as a power source for portable devices, HEV and EV. Cathode materials in LIBs are important in determining the electrochemical properties. Currently, layered $LiMO_2$ and spinel LiM_2O_4 (M = Co, Mn, Ni) have been researched as cathode materials for commercialized LIBs. But, in case of typical layered $LiCoO_2$ or spinel $LiMn_2O_4$, it is difficult to applicate in large-scale batteries due to high cost and toxicity or dissolution of manganese into electrolyte at an elevated temperature, respectively. On the other hand, polyanion-type materials ($LiFePO_4$, $LIFeSO_4F$, $LiMnPO_4$, $LiCoPO_4$, and $Li_3V_2(PO_4)_3$, etc.) possess high thermal and chemical stability, suggest interesting possibilities for large-scale batteries.

Among these materials, $Li_3V_2(PO_4)_3$ (LVP) has high operating voltage and high reversible capacity (theoretical capacity of $197mAhg^{-1}$). LVP with a NASICON (sodium super ionic conductor)-type structure enables Li^+ ions to diffuse rapidly through a three dimensional pathway of open structure. In addition, NASICON-type structure are known as thermally and chemically more stable materials than above materials because of strong covalent bonding between P and O. However, LVP is not good at high current rate due to low electric conductivity. The carbon coating is needed to improve electric conductivity of LVP. Also, various transition metals (Fe, Ti, Mn, and Co, etc.) were doped to improve electrochemical properties such as capacity, cycleability and rate capability.

In this study, LVP was synthesized by a microwave-assisted sol-gel method and was doped with transition metals for improving electrochemical properties. Microwave heating is process whereby microwaves produced by magnetrons are directed toward reactants or heating medium, which absorb the electromagnetic energy volumetrically to achieve self-heating uniformly and rapidly. LVP is synthesized using V_2O_5, $NH_4H_2PO_4$, Li_2CO_3 and oxalic acid as starting materials, various compounds containing transition metals and CNT (carbon nano tube) were used for metal doping and carbon coating, respectively. Oxalic acid and V_2O_5 in a stoichiometric ratio are dissolved in deionized water under magnetic stirring. $NH_4H_2PO_4$, Li_2CO_3 and compounds containing transition metals were added when solution is formed of a clear blue, and the mixed solution was stirred at thermostatic plate to obtain the dark blue gel. The obtained gel heated at 400℃ for 10min. After grinding, and heated again at 750℃ for 10min under Ar atmosphere. The LVP sample was obtained through the above experimental procedure.

Tuning of the diazonium electrografting using radical scavenger

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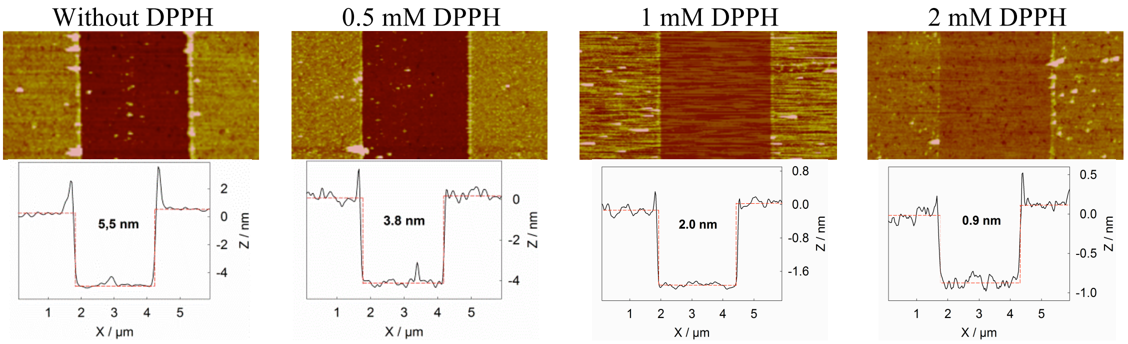
Grafting of organic structures using the diazonium chemistry is a well-known method for obtaining functionalized surfaces.[1] Various conducting materials as metals and carbon can be modified in aprotic or aqueous media, and provide covalently tethered layers. The efficiency of this grafting process rests upon the high reactivity of the aryl radicals produced at the electrode-solution interface. This reactivity leads to the generation of polyaryl layers via the radicalar attack of already grafted aryl species on the surface. As a consequence, the method routinely provides disordered organic films having a thickness varying from one to fifty nanometers. The lack of control, in terms of thickness and organization, represents the major drawback of this elegant and versatile technique.

A simple strategy to avoid the formation of polyaryl layer during the functionalization of carbon surface by diazonium reduction has been recently developed by our group.[2,3] The approach proposes to directly act on the polymerization mechanism by using a radical scavenger (DPPH = 2,2-diphenyl-1-picrylhydrazyl). The kinetic gap between the surface coupling and the multilayer formation is exploited to prevent the growth of the layer without interfering with the grafting. By modulating the DPPH concentration, the layer thickness can be tuned, as evidenced by atomic force microscopy (see below figure)[4]:



Originally achieved with the well-known 4-nitrobenzene diazonium salt, the method has been tested with several diazonium salts in order to evaluate the versatility of the approach. The grafting control was found very efficient for diazonium substituted by electron withdrawing group and less efficient for those bearing electron donating group. This result suggests that non radical polymerization mechanisms, as electrophilic substitution reactions, could play an important role in the formation of multilayered films.

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Evaluation of Polymer –Carbon Composite Supercapacitor Electrodes in Aqueous Electrolyte

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Abstract: The growing demand for portable systems, digital communication devices and electric vehicles has prompted considerable interest in supercapacitors with high power density, long cycles and high energy density. Composite formation from the conducting polymer with carbon material improves the cycle life of the conducting polymer and capacitance of the carbon material. Preparation of nano thin polypyrrole (PPy) was carried out by chemical oxidative polymerization of the monomer in 20% aqueous methanol having vapor grown carbon fibers(VGCF) already dispersed in it. The surface characterizations of the nanocomposites were done using scanning electron microscopy (SEM) and scanning transmission emission microscopy (TEM). Cyclic voltammetric (CV) measurements for half-cells made of VGCF, bulk PPy and different composites (PV) were conducted in a potential range −0.9 to −0.1V in 1 M KCl(aq) electrolyte to examine the electrochemical characteristics. Results of this study showed that nano-thin PPy layer below ~10 nm exhibited a more reaction dominant behaviour and very fast reversibility so that most mass of the PPy for this composite could contribute to the pseudo-capacitive charge storage. Using 1M KCl(aq) electrolyte, the specific capacitance of active material (PPy) was obtained as ~240Fg^{-1} at 30mVs^{-1} and maintained ~175Fg^{-1} at a higher scan rate of 200mVs^{-1}. The cyclic life test of composite electrode was performed by CV cycling over 8000 cycles. A total loss of about 20% of the initial capacity was found in first 300 cycles.

Keywords: Nano-composite films, polymerization, polypyrrole, Pseudo-capacitance, Composite electrode, supercapacitor.

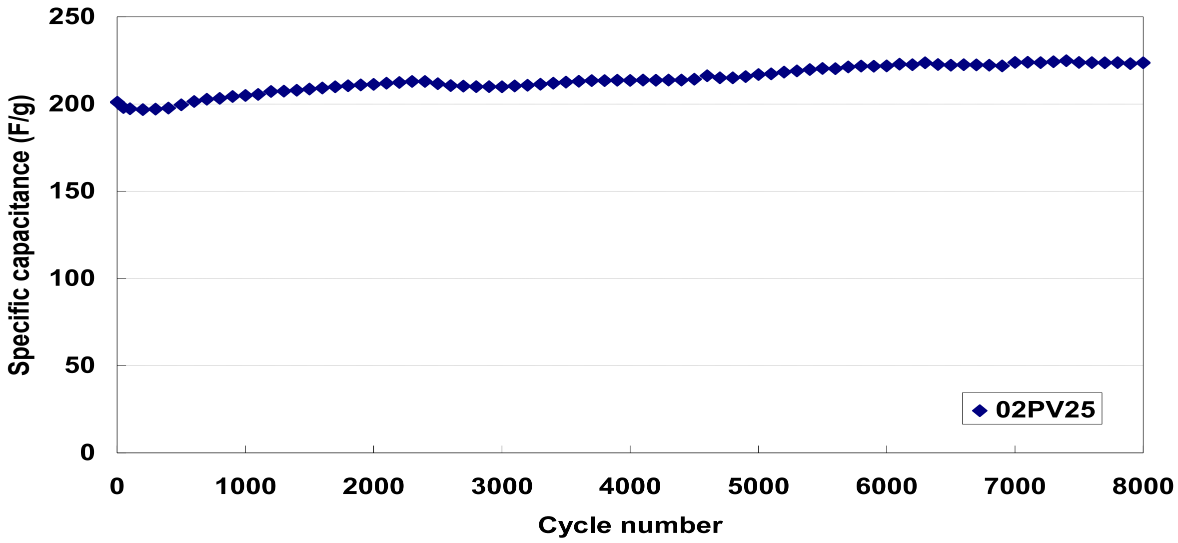

Fig. Cycle life test: @active material MSC30 + PPy; Scan rate: 20mV/sec.

Electroanalytical performances of electrodes modified with porous layers of carbon nanotubes or ion-exchange polymers

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In the last years, electroanalysis has witnessed a great growth in the employment of carbon nanotubes (CNTs) layers and/or in the use of polymer films to develop "chemically modified electrodes" [1-2]. The final devices present better electroanalytical performances, particularly in terms of peak current increase and of voltammetric peak separation narrowing, useful features for increasing selectivity and sensitivity and for lowering detection limits.

The better performances are not only to be searched in a change of electrode kinetics (*e.g.* catalytic effects brought by nanomaterials or their functionalization, decrease in charge transfer resistance) or in an increment of surface area or porosity distribution, but also in an analyte adsorptive preconcentration capability and in a change of the mass transport regime, from planar to convergent or to thin-layer [3-4].

In this presentation, we would like to contribute to this debated topic, with some experimental results obtained working with different modified electrodes:

1) electrodes modified with appropriately functionalized CNTs;
2) electrodes modified with Sulphonated Poly (Aryl Ether Sulphones), a new class of polymers, *ad hoc tailored* for electroanalytical applications;
3) electrodes modified with polyamidoamines and cyclodextrins;
4) electrodes modified with electrospun polymers.

The above mentioned modifications have led to a general increase in the analyte adsorption capabilities and in the film mesoporosity which, also according to theoretical studies [4], is the responsible of the transition from the linear diffusion regime to the thin-layer behavior. Both phenomena cause the enhancement of the peak currents, improving sensor performances.

Optimization of the sensor devices for the detection of some contaminants of emerging concern (*e.g.* benzidines, o-toluidine, tolidine, halothane) and their application in real-world analytical cases are also presented and discussed.

ACKNOWLEDGEMENTS
This work has been supported by Fondazione Cariplo (Milano, Italy), grant no. 2014-1285.

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Bipolar Electrochemistry in Materials Science

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The concept of bipolar electrochemistry allows to electrochemically address objects that are not physically connected to an electrode.[1,2] By placing conducting objects in an electrolyte under the influence of an electric field they will exhibit an anodic and a cathodic part, and therefore are called bipolar electrodes. The electric field will induce a potential difference between the object and the surrounding solution with the consequence that both, oxidation and reduction reactions, occur simultaneously at the opposite sides of the same electrode. This particularity has been used to produce asymmetric objects know as Janus or patchy particles. Bipolar electrochemistry is an interesting approach to produce asymmetric particles, because in contrast to most of the classical methods employed to produce this type of particles, it is possible to synthesize them in the bulk of a solution. This allows a 3D production instead of using an interface or a surface to break the symmetry, which implies a 2D production, and therefore a lower time-space yield. Therefore bipolar electrochemistry might be suitable for the industrial production of large amounts of asymmetric particles. There is a variety of materials that can be used as substrate, especially some allotropes of carbon, but also different types of metals and also some semi-conductors.

Metals (Au, Cu, Pt…), polymers (polypyrrole, polyNIPAM…) and organic layers obtained from amine oxidation and/or diazonium reduction have been deposited using bipolar electrochemistry.[3] We also used the concept of indirect bipolar deposition to generate different types of materials. In indirect bipolar electrodeposition the redox reaction on the bipolar electrode surface will induce a second chemical reaction which will modify the surface of the bipolar electrode. The most common indirect electrodeposition mechanism implies local pH changes triggered by bipolar electrochemistry.[4] It is also possible by a fine control of the polarization potential along the surface of the object to obtain a gradient of thickness and/or composition.[5]

These particles open up promising perspectives for applications in different areas ranging from molecular electronics to targeted drug delivery.

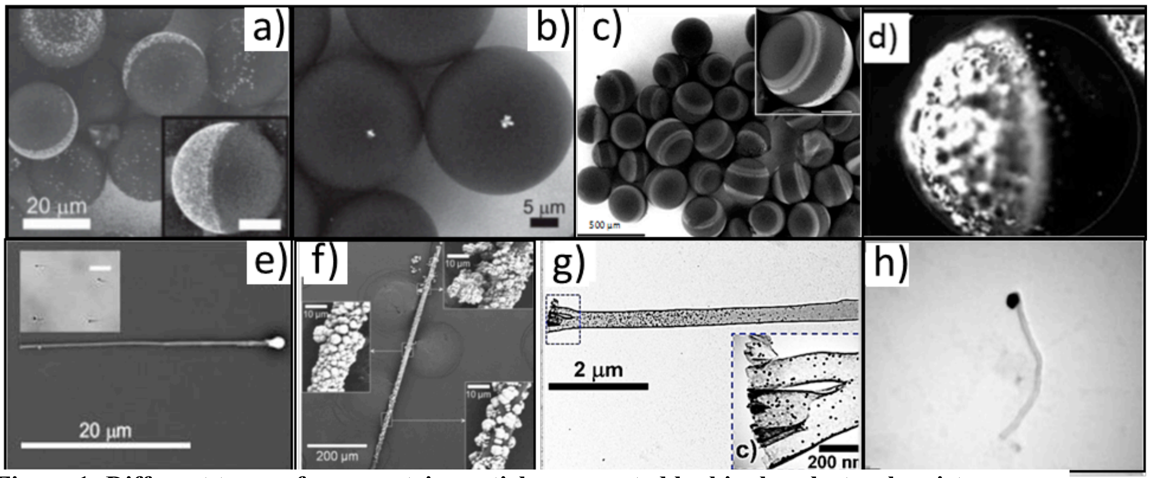

Figure 1: Different types of asymmetric particles generated by bipolar electrochemistry

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Local generation of TiO_2 and SECM screening of photoelectrochemical activity

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Surface patterning by scanning electrochemical microscopy (SECM) represents a new tool for a large variety of analytical applications and electronics development. Titanium dioxide is one of the most investigated compounds in materials science due to its unique properties that enable its use in a wide variety of applications such as solar cells and photocatalysis.[1] In this work, we present the localized growth of TiO_2 by anodization of a titanium surface, confined to a micro-sized region and the use of a combined optical fiber-SECM for the screening of their photoelectrochemical properties for water splitting.[2] The localized anodization of a Ti substrate was performed using a combine micropipette-microelectrode system. The electrolyte was locally deposit on the surface through the micropipette and the microelectrode was used as the cathode (figure 1.a). A local spot containing TiO_2 was hence obtained. The advantage of this localized anodization is the possibility to obtain on the same Ti substrate TiO_2 spots with different photocatalytic properties obtained by varying the anodization potential and the TiO_2 growth time. A high-throughput screening of the photoelectrochemical properties of these spots was achieved by locally illuminating the surface with UV light provided a combined optical fiber-gold microelectrode tool (figure 1.b) that allows simultaneous measuring of water oxidation photocurrent and reduction current of the produced oxygen (figure1.c). The oxidation current associated with water splitting was recorded on the entire substrate and hence the photoelectrochemical activity of each spot could be imaged.[3] A direct correlation was obtained with the morphology of each spot obtained from SEM analysis.

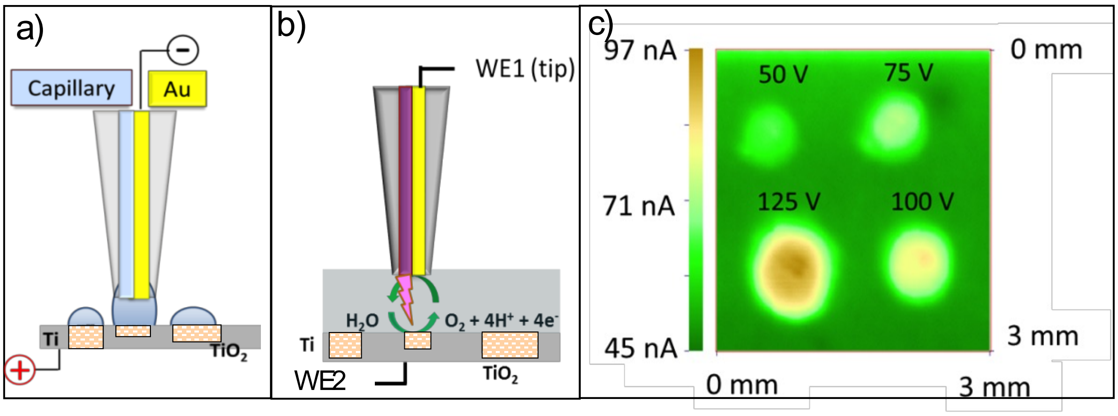

Figure 1: a))Scheme of the local anodization of Ti plate for the generation of multiple TiO_2 spots. b) Simultaneous screening of TiO_2 spots for photoelectrochemical water oxidation and for oxygen reduction using the OF-UME tool. c) SECM image of TiO_2 spots produced with Cap-UME tool at different anodization potentials

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Carbon Monoxide, Formic Acid and Ethanol Electrooxidation on Pseudomorphic Noble Metal Layers and Nanoalloys

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In electrooxidation of small organic molecules, such as ethanol and formic acid, noble metals exhibit exceptional catalytic activity. However even for the most active catalysts known, both above mentioned reactions proceed with high overpotentials at room temperature. The overall low activity of known catalysts towards electrooxidation of organic molecules render the low temperature fuel cells fed with liquid organic fuels, such as direct ethanol fuel cells, far from being economically viable.

Better understanding of the factors influencing catalytic activity is crucial to design new, more active catalytic systems. It is widely accepted that catalytic and electronic properties of catalyst‘s surface are strongly related. Electronic properties of catalyst can be purposely modified, for instance by modifying its lattice parameter. In general, changes of the lattice parameter of metals will induce changes in their electronic properties as degree of overlapping of band forming orbitals change. As a result, when metal lattice is contracted, the valence band becomes broader, and when metal lattice is expanded the valence band (d-band) shrinks. The changes in d-band width causes the shift of the d-band: the broadening of the valence band leads to shift of the d-band center away from Fermi level and when the d-band shrinks, the d-band center shifts in the opposite direction [1]. The changes in d-band center position relative to Fermi level can be correlated to adsorption properties of the surface [1]. We used the above mechanism to purposely induce the changes in the electronic properties and to investigate how the changed electronic properties influence the catalytic activity.

To study the correlation between electronic and electrocatalytic properties of catalysts we used two distinct types of model systems: i) epitaxial layers of catalytically active noble metals (platinum, palladium) on another noble metals and ii) nanoalloys, where catalytically active metal was alloyed with metal inactive towards the studied reaction, such as Pt-Pd which we used for electrooxidation of ethanol in acidic conditions. In those conditions palladium is catalytically inactive, and also does not participate in so called “bi-functional mechanism”, thus it can be assumed, that the overall catalytic activity can be to a large extend attributed to changes in surface geometry and to changes of electronic properties of platinum.

We also studied carbon monoxide and formic acid oxidation. Carbon monoxide oxidation is an important reaction as CO is a common by-product when organic molecules are oxidized, and because CO strongly adsorbs on the surface of the catalyst usually significantly decreasing its catalytic activity. It is also a good probe to investigate the changes in chemisorption energy and correlate it to changes in catalytic activity. Formic acid can also play a similar role, as its oxidation on Pd follows a simple, direct oxidation pathway to CO_2, thus providing more insight on electronic properties of the surface.

To confirm changes in the electronic properties of our catalysts we used X-ray Photoelectron Spectroscopy (XPS) and UV Photoelectron Spectroscopy (UPS). D-band and core-level spectra allows for determination of the electronic properties of the material, and together with electrochemical results the relation between electronic and electrocatalytic properties can be studied. Establishing the link between catalytic and electronic properties of the surface would allow for better understanding of the catalytic processes and the role of the electronic properties in the overall catalytic activity. This could direct the search towards most promising systems, and as a result new, more active catalytic materials can be synthesized.

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Modified & Functional liquid-liquid interfaces

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For many years, our laboratory has been active in elucidating the electrochemical aspects of charge transfer reactions at polarized liquid-liquid interfaces, including ion transfer, assisted ion transfer and heterogeneous electron transfer reactions.

These interfaces can be chemically modified in many ways.

Molecular catalysts: The adsorption of molecular catalysts such as porphyrins can be used to drive reactions such as oxygen reduction. The results obtained by a series of porphyrins will be presented.

Nanoparticles: The adsorption of gold nanoparticles can also be used to catalyse the reduction of oxygen at soft interfaces using an aqueous electron donor such as ferrocyanide. The adsorption of gold nanoparticles yield the formation of films with very interesting optical properties such as mirrors or filters. Both the electrochemical and optical features will be discussed.

Functional rafts: Soft interfaces can be modified by carbon nanotubes (CNT), graphene oxide, etc.. decorated with nanoparticle catalysts. For example, floating rafts made of CNT decorated with Molybdenum Carbide nanoparticles are very efficient at catalyzing hydrogen evolution at the interface between an aqueous acidic solution and an organic solution containing an electron donor such as decamethylferrocene.

All in all, we shall discuss of modified liquid interfaces could find applications in photo-induced water splitting reactions.

Nitrogen-doped Mesoporous Carbon Coated MWCNTs for Lithium Sulfur Batteries

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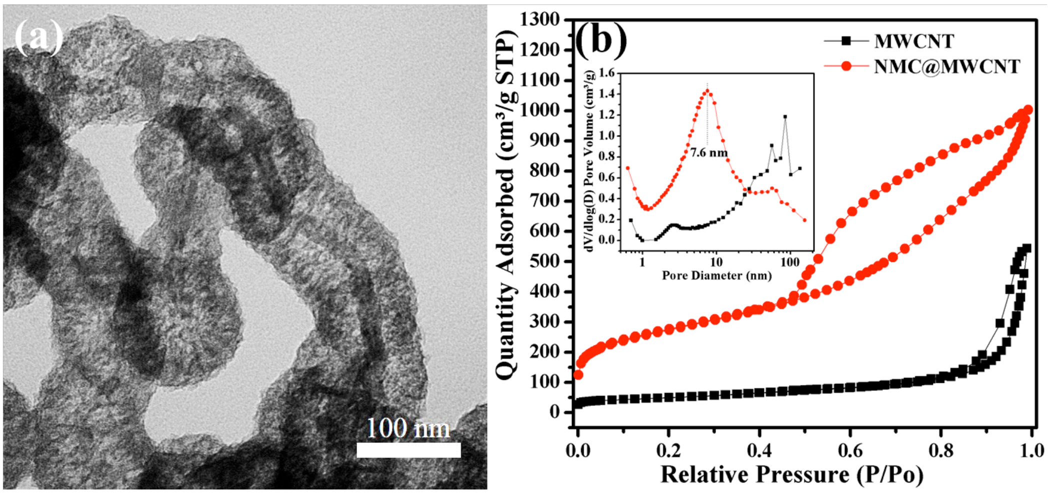
In order to address the ever-growing problems of fossil depletion and environmental pollution, it is an urgent need to develop high capacitive energy storage systems. Recently, there has been an intensive research on lithium-sulfur (Li-S) batteries due to their high theoretical capacity (1672 mAh g^{-1}).[1, 2] However, due to the low conductivity of sulfur and the occurrence of shuttle effect, the rate capability of the batteries is limited.[3] Encapsulating sulfur into porous carbon has been proved as an effective approach to solve this problem, due to the good conductivity and high specific surface area of porous carbon.[1][4] Carbon nanotube (CNT) has been used as the host for encapsulating sulfur because of its good conductivity and porous structure.[5] However, the relatively low specific surface area and poor porosity of CNT limit the accommodation and direct contact between sulfur and electrolyte, leading to inevitable dissolution of lithium polysulfide.[6] Therefore, it is logic to coat a high specific surface area of porous carbon on the surface of CNT to improve the accommodation of sulfur. Herein, a novel and facile interfacial sequential heterogeneous nucleation pathway way were demonstrated to provide multi-wall CNT (MWCNT) with a nitrogen-doped porous carbon coating. Benefiting from the fact that nitrogen can promote oxygen-containing functional groups chemically bonding with sulfur, the distribution of the loaded sulfur was uniform and the dissolution of polysulfide could be greatly prevented. The relationship between pore size, thickness of the carbon coating and battery performance will be investigated.



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Layered Transition Metal Dichalcogenides as Electrocatalysts for Hydrogen Evolution and Their Trends Emerging from Electrochemical Treatment

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Layered transition metal dichalcogenides (TMDs) are thrust into the limelight within the scientific community thanks to their properties that can be exploited for a myriad of applications in electrochemistry and electrocatalysis of hydrogen evolution reaction (HER). Of interest, we investigate the correlation between electrochemical treatment of exfoliated MoS_2, WS_2, $MoSe_2$ and WSe_2 nanosheets in the hopes of electrochemically activating their electrochemical and electrocatalytic properties. In the electrochemical aspect, we show that electrochemical activation is achieved, for all TMDs except WS_2, via electro-reduction at selected reductive potentials based on their innate electrochemistry while all TMDs become electrochemically deactivated upon electro-oxidation. Across all TMDs, $MoSe_2$ exhibits most prominent charge transfer activation. Scrutinizing further, we conclude that molybdenum metal and selenium chalcogen type are more prone to electrochemical activation than tungsten metal and sulfur chalcogen type. Contemporary research into TMDs as prospective electrocatalysts for hydrogen evolution has been overwhelming; driven by the ardent pursuit of cheaper alternatives to the rare precious metal platinum, which is the best electrocatalyst to date. TMDs are abundant in nature and also exhibit promising electrocatalytic performance for HER. It provides an interesting perspective to explore the influence of electrochemical potential on the efficiency of the TMDs as a HER electrocatalyst. We found that MoS_2 demonstrated better HER performance upon electro-reduction whereas the electro-oxidation of WS_2 deteriorated the HER performance significantly. Conversely, the HER efficiency of $MoSe_2$ and WSe_2 remained largely unperturbed by electrochemical pretreatment. Therefore, in terms of HER electrocatalysis, we conclude that sulfur-containing TMDs are more receptive to electrochemical redox treatment compared to selenium-containing TMDs. These findings are advantageous towards the electrochemistry of TMDs and provide insights into the effectiveness and feasibility of electrochemical activation for charge transfer and HER electrocatalysis applications. The administration of such knowledge to electrochemical and energy applications in future will be indefinitely beneficial.

Electrochemistry of Anti-MoS_2 Structure: Tl_2S

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Presently, scientists have been ramping up research into low-dimensional materials that exhibit high anisotropy. In particular, the layered transition metal dichalcogenides represent a class of such materials that has garnered much success for electrochemical applications in sensing, energy storage and generation. Despite the hype over layered transition metal dichalcogenides like MoS_2 and WS_2, other layered metal chalcogenides; beyond the transition-metal group, have received little attention from the scientific community. One such example is thallium(I) sulfide (Tl_2S), a Group 13 chalcogenide, which adopts the peculiar anti-$CdCl_2$ type structure where the chalcogen is sandwiched between the metal layers. The structure of Tl_2S is a complete opposite of frequently studied transition metal dichalcogenides including 1T-MoS_2 which has a regular $CdCl_2$ structure. The electronic structure of Tl_2S thus differs from MoS_2. Such structure may provide a useful insight and understanding toward its electrochemical behavior in relation to the electrochemical properties of MoS_2. Herein, we investigated the inherent electrochemistry of Tl_2S and its implications for sensing and energy generation, specifically the electrocatalytic properties toward the hydrogen evolution reaction (HER). We show that Tl_2S manifests four distinct redox signals at *ca.* 0.4 V, -0.5 V, -1.0 V and -1.5 V *vs.* Ag/AgCl as a result of intrinsic oxidation and reduction of the material when an electrochemical potential is applied. We also demonstrate that Tl_2S has slow electron transfer abilities with a rate (k^0_{obs}) as low as 6.3×10^{-5} cm s^{-1}. The poor conductivity of Tl_2S renders the HER electrocatalytic behavior second-rate compared than MoS_2. Furthermore, we investigated the electronic properties of Tl_2S and found that Tl_2S exhibits unusually narrow band dispersion around the Fermi level. Hence, an awareness of Tl_2S electrochemistry unveils interesting features of anti-MoS_2 structures in field of the layered transition dichalcogenides.

Ultrasensitive Detection of Chiral Molecules by Tunneling Current through Gold Nanoparticle Networks

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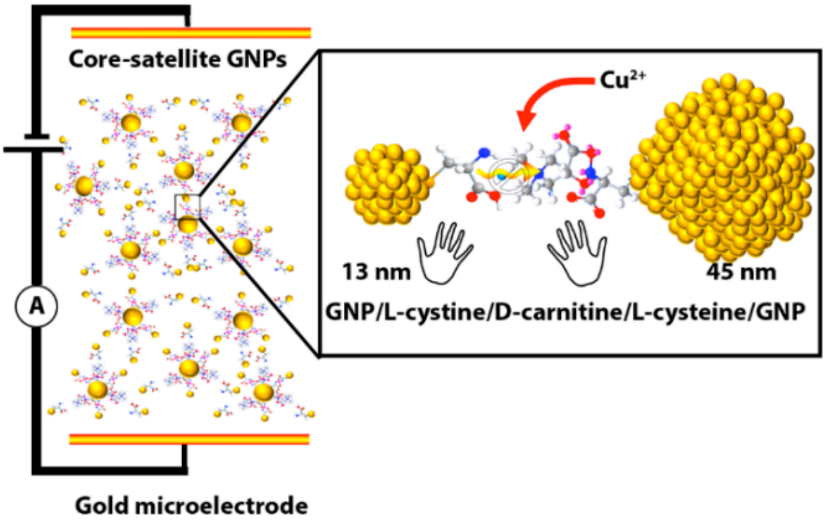
The recent developed recognition tunneling technique has demonstrated that the binding between recognition molecules and target molecules in a molecular tunnel junction can generate unique and sensitive changes in tunneling current and the changes can be used to identify target molecules at the single molecule level. We report a novel method for ultrasensitive detection of chiral molecule L/D-carnitine based on changes in the recognition tunneling current across self-assembled core-satellite gold nanoparticle (GNP) networks functionalized with amino acid (L-cysteine). The exposure to D/L-carnitine suppresses the tunneling current through the L-cysteine modified GNP networks. The replacement of D/L-carnitine by copper ions recovers the tunneling pathways and generates a significant decrease in the resistance of the networks. The normalized resistance change is extremely sensitive to the chirality of carnitine molecule, which is originated from the different binding strength between homo- or heterochiral pairs. The small difference in the binding strength is amplified by the tunneling current through the large number of tunneling junctions in the GNP networks. The GNP networks are thus ultrasensitive to trace level chiral molecules and can be used to differentiate the L- or D-carnitine molecules.



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Enhanced efficiency of dye-sensitized solar cells with trench structured TiO_2 nanoparticles photoelectrode

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Compared to the high cost industrial Si solar cells, the dye-sensitized solar cells (DSSCs) have attracted much attention because of low cost, efficient, and simple fabrication process. DSSCs consist of a TiO_2 anode electrode and a Pt counter electrode, with the dye and electrolyte between them. The TiO_2 nanoparticles (NPs) based DSSCs device has shown the efficiency over ~10% using high-cost FTO coated glass substrate. Many researches for flexible DSSCs using Ti substrates have been performed to extend the applications of DSSCs. However, NP-DSSCs using the Ti substrate show much lower efficiency than DSSCs using the FTO-glass substrate because the incident light toward the counter electrode is absorbed by the electrolyte.

In this study, we have applied the trench structured TiO_2 NPs photoelectrode to improve the cell efficiency of conventional TiO_2 NPs based DSSCs using Ti substrate. The trench-type TiO_2 NP-DSSCs (TiO_2 NPs trenched in Ti foil) have more charge transport paths than do standing-type TiO_2 NP-DSSCs (TiO_2 NPs on Ti foil) due to the increase of contact area between the TiO_2 NPs sidewall and the Ti foil. The increase of contact area decreases the electrical resistance and increases the charge collection efficiency, which leads to the improvement of Jsc. Therefore, compared to the conventional standing-type TiO_2 NP-DSSCs, the trench-type TiO_2 NP-DSSCs have shown an approximately 30% improvement in power conversion efficiency because of the improvement of Jsc.

Improvement of Electrochemical Performance of Bilayer SOFC Electrodes Formed by EPD

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It is well known that solid oxide fuel cells (SOFCs) are the next-gen hydrogen fueled power generator, because of their high energy conversion efficiency and fuel adjustability. In order to achieve high electrical performance of SOFC, the lowering of the overpotentials of both electrodes, cathode and anode, is indispensable as well as the lowering of ohmic resistance of electrolyte. Up to date, much effort has been paid for developing electrode material with low overpotential. For instance, perovskite-type oxide with high electronic and oxide-ionic conductivities [1] and Ni-YSZ cermet with highly active Ni catalyst [2] are commonly used as cathode and anode of SOFCs, respectively. We previously succeeded in forming double layer cathodes consisting of LSM-YSZ as the active layer and LSM ($La_{0.8}Sr_{0.2}MnO_3$) as the current collecting layer (LSM-YSZ/LSM) by electrophoretic deposition (EPD) technique [3]. In the present study, EPD method was applied to fabricate anode and cathode of SOFCs and the resulting cell was evaluated in SOFC performance.

The monolayer and bilayer electrode films were formed by the EPD technique, as described elsewhere [3]. The film thickness of each layer was controlled by changing applied voltage and deposition time of EPD. H_2-O_2 SOFC performance was measured for the cell with the resulting electrodes.

The bilayer anode films consisting of 50wt%Ni-YSZ (50Ni-YSZ) and 70wt%Ni-YSZ (70Ni-YSZ) were formed using EPD technique. For the monolayer anode, the 70Ni-YSZ was superior to the 50Ni-YSZ in its anodic property. However, the formation of the 50Ni-YSZ/70Ni-YSZ bilayer gave a significantly higher anodic property compared to the monolayer anodes. This result suggests that the 50Ni-YSZ, which has a lower Ni content, possesses a greater number of reaction sites due to its higher Ni dispersion compared to the 70Ni-YSZ, and the addition of the 70Ni-YSZ layer effectively enhanced the anodic property. Since the 70Ni-YSZ layer has a porous structure, it functions as a good gas diffusion and current collecting layer. The critical thickness of the 50Ni-YSZ as an active layer was 3 μm in the present anode structure.

The bilayer cathode films, LSCF/YSZ, LSCF/GDC and LSCF-GDC/GDC (LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$, GDC: $Gd_{0.1}Ce_{0.9}O_{1.95}$), were prepared by EPD technique. The bilayer cathodes exhibited significantly higher properties compared to the LSCF single layer cathode. The formation of the interlayer was effective to enhance the cathodic property. In spite of the formation of $SrZrO_3$ insulating phase, the LSCF/YSZ exhibited even higher property in its initial property than the LSCF/GDC. We tentatively assign this result that EPD formation of the LSCF/YSZ bilayer gives a thermally stable interface between LSCF and YSZ. However, long-term heating at 1100 ^{o}C for 100 h, the LSCF/YSZ bilayer significantly deactivated. On the other hand, the LSCF/GDC bilayer did not change in its property. The EPD technique using the mixed suspension of LSCF and GDC successfully gave LSCF-GDC composite cathode on the GDC interlayer. The LSCF-GDC/GDC bilayer cathode was superior to the LSCF/YSZ and the LSCF/GDC cathode in its initial property and long-term stability.

In conclusion, it was found that EPD technique significantly improved the interface between electrolyte and electrode (anode and cathode) of SOFC, resulting in the lowering of the electrode overpotential and the achievement of long-term stability.

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(Metallo)-Proteins and Enzymes in Bacteria at Modified Electrodes as Stable and Living Catalysts in Microbial Fuel Cells

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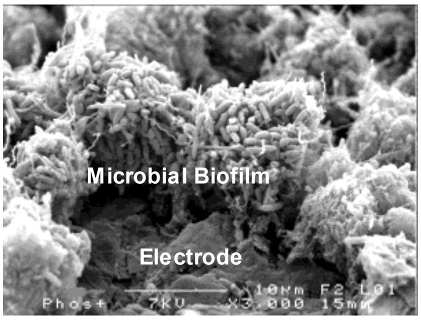
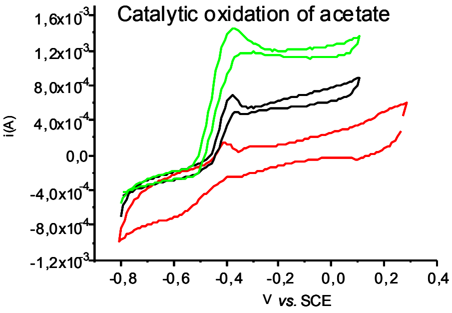
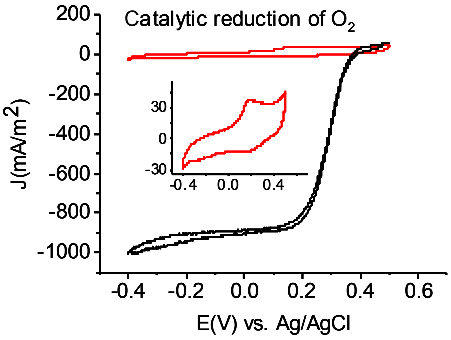
The reductionist biomimetic synthesis of active sites of enzymes often fails to produce simple artificial catalysts that compete with the performance and selectivity of enzymes.[1] The direct use of extracted and isolated enzymes at electrodes is possible but suffer from poor catalytic stability in time.[2] This paper will discuss the use of living micro-organisms at electrodes as catalysts in fuel cells (SEM micrograph figure left).[2] We will address the underlying metabolic mechanisms for exo-cellular electron transfer at anodes[3,4] (*e.g.* oxidation of acetate, figure center) and at cathodes[5,6] (reduction of dioxygen, figure right). One of our interests in the field of bioelectrochemical systems is the tailoring of the microbial-electrode interface through surface grafting in order to improve the development of electroactive biofilm and its electrical connection.[3,4] Several examples of surface modification involving electrostatic or more specific interactions will be presented. Perspectives in energy conversion such as microbial fuel cells will be put forward.[7]







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Facile electrochemical fabrication of nanostructured amorphous $Co(OH)_2$ on gold electrodes as an efficient oxygen evolution catalyst

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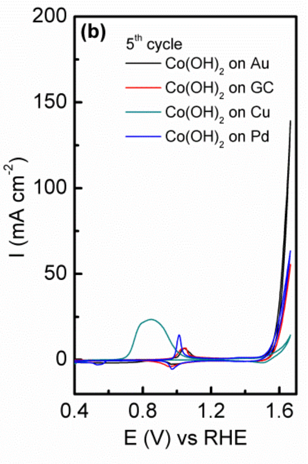
Cobalt oxides have recently been shown to be highly effective electrocatalysts for the electrochemical transformation of water to molecular oxygen under alkaline conditions. The most widely studied oxides such as Co_3O_4 and CoOOH often require an elevated temperature step during their synthesis to create crystalline materials [1, 2]. In this work we investigate the rapid and direct electrochemical formation of amorphous nanostructured $Co(OH)_2$ on gold electrodes under room temperature conditions which resulted in a highly effective oxygen evolution reaction (OER) electrocatalyst. Significantly, during the OER some conversion to crystalline Co_3O_4 occurs at the very surface of the material but the bulk remains amorphous. In addition it was found that the gold support was critical to such good performance as different support materials such as carbon, palladium and copper showed decreased activity (as shown in the figure). This Au/$Co(OH)_2$ catalyst exhibits excellent activity achieving a current density of 10 mA cm^{-2} at an overpotential of 360 mV with a high turnover frequency of 2.1 s^{-1} in 1 M NaOH. A Tafel slope of 56 mV dec^{-1} at low overpotentials and a slope of 122 mV dec^{-1} at high overpotentials is consistent with the dual barrier model for the electrocatalytic evolution of oxygen. Encouragingly, the catalyst maintains excellent activity for up to 24 hr of continuous operation and this electrochemical approach offers a facile and rapid way to create a highly effective and stable material.



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Nanoelectrochemical Detection of Short-Lived Intermediates of Electrocatalytic Oxygen Reduction: Elucidation of the Reaction Mechanism

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Some of us recently introduced new methodology for detecting charged reactive intermediates of heterogeneous processes and used it to investigate the oxygen reduction reaction at polycrystalline Pt. A nanometer-sized pipette filled with organic solvent immiscible with the external aqueous solution was used as a tip in the scanning electrochemical microscope (SECM) to detect and identify a short-lived superoxide intermediate and determine the rate of its generation at the catalytic Pt substrate [1]. The interpretation of that experimental data was based on a simplified model that left a number of open questions about superoxide desorption and its lifetime in neutral aqueous solution. Here we will report the results of simulations based on a more exact model (including the effect of local solution pH) and aimed at the detailed mechanistic analysis of this system [2].

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Enhanced efficiency of dye-sensitized solar cells with trench structured TiO_2 nanoparticles photoelectrode

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Compared to the high cost industrial Si solar cells, the dye-sensitized solar cells (DSSCs) have attracted much attention because of low cost, efficient, and simple fabrication process. DSSCs consist of a TiO_2 anode electrode and a Pt counter electrode, with the dye and electrolyte between them. The TiO_2 nanoparticles (NPs) based DSSCs device has shown the efficiency over ~10% using high-cost FTO coated glass substrate. Many researches for flexible DSSCs using Ti substrates have been performed to extend the applications of DSSCs. However, NP-DSSCs using the Ti substrate show much lower efficiency than DSSCs using the FTO-glass substrate because the incident light toward the counter electrode is absorbed by the electrolyte.

In this study, we have applied the trench structured TiO_2 NPs photoelectrode to improve the cell efficiency of conventional TiO_2 NPs based DSSCs using Ti substrate. The trench-type TiO_2 NP-DSSCs (TiO_2 NPs trenched in Ti foil) have more charge transport paths than do standing-type TiO_2 NP-DSSCs (TiO_2 NPs on Ti foil) due to the increase of contact area between the TiO_2 NPs sidewall and the Ti foil. The increase of contact area decreases the electrical resistance and increases the charge collection efficiency, which leads to the improvement of Jsc. Therefore, compared to the conventional standing-type TiO_2 NP-DSSCs, the trench-type TiO_2 NP-DSSCs have shown an approximately 30% improvement in power conversion efficiency because of the improvement of Jsc.

Platinum Electroless Plating of Silk Utilizing Supercritical Carbon Dioxide

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With the exceptionally fast advancement in technology over the decades, wearable devices have attracted much attention for the next generation technology. The combination of the conductive materials and the flexible fabrics, such as metal and polymer, becomes the greatest challenge. This study carried out a novel catalyzation with the assist of supercritical carbon dioxide (sc-CO_2) and the plating of Pt on silk. Electroless plating is a prevalent technology to fabricate the metal-polymer composite materials due to its eminent advantages, such as low processing temperature, low cost, and simple operation procedures [1]. Electroless plating usually involves a pretreatment step to clean and roughen the surface, a catalyzation step to deposit the catalyst seeds, and a plating step to deposit the metallic coating. Distinct from the conventional processes, catalyzing the polymer in sc-CO_2 allows exclusion of the pretreatment step and further resulting in a defect-free and smoother surface [2]. With the outstanding self-diffusivity, high compatibility with non-polar materials, and low surface tension characteristics of sc-CO_2, organo-metallic catalysts can be embedded into the polymer without damaging the structure.

There are many literatures related to the electroless plating involving Pd catalyzation and Ni plating, however, there is still no literature concerning Pt electroless plating, which is Pt catalyzation followed by Pt plating, of silk textiles. Pt electroless plating of silk is foreseen to be the most promising material for the wearable devices because of its crucially irreplaceable properties. First, the electrical conductivity of Pt is very similar to Ni, however, the ductility, a very essential demand to the wearable device, of Pt is 1.5 times better than Ni [3,4]. Second, the corrosion resistance of Pt is also eminent [5]. Third, bio-compatibility of Pt is higher than that of Pd and Ni, which is the most vital advantage for applications in wearable devices [6]. Moreover, silk is a common material in clothes, the combination of Pt and silk is thus considered to be the most potential candidate for the wearable devices. This work, therefore, executed the electroless plating between Pt and silk.

A piece of the silk textile was immersed in the sc-CO_2 fluid containing Pt(II) acetylacetonate (Pt(acac)$_2$) at 80 ^{o}C and 15 MPa. Appropriate amount of the Pt(acac)$_2$ was used to maintain the concentration at the saturation concentration throughout the catalyzation step. No pretreatment was conducted in this study. The plating step was thereupon being carried out on the catalyzed silks at 70 ^{o}C and atmospheric pressure in the Pt alkaline solution. Various lengths of plating times were performed to inspect the relationship between the plating time and the properties. The surface morphology, cross-section and composition were examined by an optical microscope (OM), scanning electron microscope (SEM), and energy dispersive X-ray spectroscopy (EDX). The phase and crystal structure were analyzed by an X-ray powder diffractometer (XRD). The conductivity was measured by the four-probe method.

By conducting the catalyzation in sc-CO_2, smooth and uniform coverage of Pt was successfully electroless plated on the silk textiles under various lengths of the plating times. The coating on the silks have been confirmed to be metallic Pt phase through the XRD patterns within the detection limitation.

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Electrospun PVdF Nano Fiber Web as Separator for Lithium Ion Batteries

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Electrospun nanofiber web is highly attractive as a separator for lithium ion batteries because of its high electrical, thermal, chemical and mechanical properties. In moving toward wider battery applications of the nanofiber separator, a deeper understanding on the structure and property relationship is highly meaningful. In this regard, we prepared electrospun poly(vinylidene fluoride) (PVdF) webs with various thickness (10~100 μm) and investigated their electrochemical performances. As the thickness of the web was decreased, a decrease of porosity and an increase of pore size were resulted in. Also, the thinner separators exhibit faster electrolyte wetting and smaller interfacial resistance. However, the discharge capacity, rate capability, cycling stability, and temperature stability were highest at an intermediate thickness of 30 μm, stressing the importance of absolute amount of electrolyte uptake.

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Synthesis and high lithium-ion conductivity of Al-doped cubic garnet $Li_7La_3Zr_2O_{12}$ (LLZO)

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Al-doped cubic $Li_7La_3Zr_2O_{12}$ (LLZO) was successfully synthesized by a sol-gel method and electrochemically characterized. Polycrystalline powders of c-LLZO were prepared from the molecular mixtures of lithium Nitrate, lanthanum nitrate, zirconium nitrate and aluminum nitrate and subsequent annealing of the dried precursor sol at 900□ for 2 h in air condition.

Phase formation was studied by X-ray powder diffraction. Al doping was necessary for the preparation of cubic LLZO ceramics crystallizing and found to facilitate the formation of the cubic garnet modification at lower synthesis temperature. The ionic conductivity of cubic LLZO was found to increase by Al doping. The highest ionic conductivity in room temperature of cubic LLZO was 0.2 mS cm^{-1}.

A C^{+4} ion beam irradiated MWCNT/AuNPs composite sensor for a sensitive assay of purine nucleosides of DNA

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A novel electrochemical sensor based on irradiation of MWCNT/AuNPs composite by high energy carbon ion beam has been developed for the determination of deoxyguanosine (dGuo) and deoxyadenosine (dAdo). The sputtering of carbon atoms has been found to breaks the basic symmetry of nano-composite and contribute to increase in the rough surface, reactivity and conductivity of nano tubes thin film. The high energy carbon ion beam irradiated MWCNT/AuNPs/GC sensor was found to show a strong synergistic electrocatalytic effects towards the oxidation of dGuo and dAdo. The morphology of the sensor was studied by using Raman spectroscopy, Field Emission-Scanning Electron Microscopy (FE-SEM) and Electrochemical Impedance Spectroscopy (EIS). The electrochemical performance of the irradiated MWCNT/AuNPs/GC sensor was investigated by using cyclic voltammetry and square wave voltammetry. The irradiated sensor has been found to exhibit an excellent electrocatalytic activity, leading to an enhancement in the peak currents of dGuo and dAdo. The peak potentials also shifted to less positive potentials as compared to the unirradiated MWCNT/AuNPs/GC (pristine). These results indicate that irradiation by carbon ion beam induced defects in the nanostructure lattice and hence, accelerate the rate of electron transfer and catalyze the electro-oxidation of dGuo and dAdo. The peak current of dGuo and dAdo was found to be linear in the range of 1–500 mM and detection limits of 126 and 109 nM, respectively, were observed. The impact of other experimental conditions on the electrochemical oxidation of dGuo and dAdo such as scan rate, frequency and pH was also measured. It is found that the oxidation of both the deoxy compounds followed an adsorption controlled pathway and the equal number of protons and electrons were involved in the oxidation. Further, the presence of various interferents like uric acid, xanthine, guanine, adenine, thymine and cytosine was examined on the determination of dGuo and dAdo. From the observed results, it was inferred that the irradiated sensor can be safely applied for the simultaneous determination of dGuo and dAdo in the biological fluids, urine and serum without facing difficulty even if common interfering species present. The practical utility of the irradiated sensor has been demonstrated by the determination of dGuo and dAdo in the DNA samples extracted from herring sperm and a MCF7 cell line (human breast cancer cells).

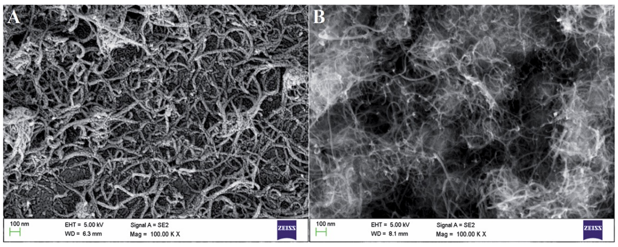

Fig. 1 Comparative FE-SEM images observed for (A) pristine MWCNT/AuNPs/GC and (B) irradiated MWCNT/AuNPs/GC.

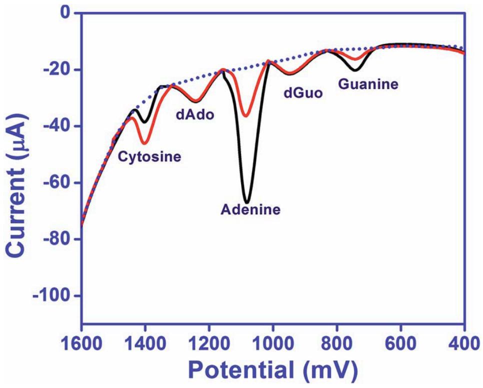

Fig. 2 Typical voltammograms showing interference of guanine, adenine, thymine and cytosine at fixed concentration (100 µM) of dGuo and dAdo.

Facile preparation hybrid material of $CoFe_2O_4$/graphene for anode in sodium ion batteries

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ABSTRACT—Sodium-ion batteries (SIBs) have emerged as a potential low-cost electrochemical system for large-scale energy storage recently. Targeting with the goal to find low-cost electrode materials and easily large-scale product process, herein, one popular kind of spinel ferrites of $CoFe_2O_4$ was explored for SIB electrode. Hybrid materials of $CoFe_2O_4$ nanoparticles anchoring on graphene as anode material for SIB are prepared by a facile hydrothermal process. The hybrid structure not only could separate graphene to be favourable for ion transport and diffusion, but also could be used as conductive matrix to improve the material electrical conductivity. The hybrid material anode displays an excellent performance with a large reversible capacity of 330 $mAhg^{-1}$ after 75 cycle times and good rate capability of 170 $mAhg^{-1}$ at 1 Ag^{-1}.

Design of Active and Durable Catalysts with Non-precious Materials for oxygen reduction and Evolution Reactions: First Principles Prediction and Experimental Validation

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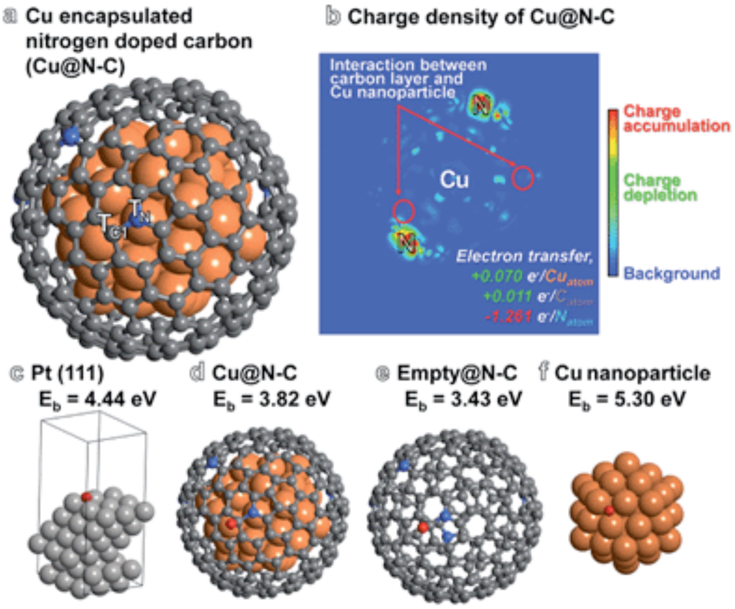
Using first-principles density functional theory (DFT) calculations and experimental materialization, we design highly active and durable catalysts toward oxygen reduction reaction (ORR) with nonprecious Cu@N-C materials. DFT calculations indicate that encapsulated Cu metal by N-doped carbon shells is a promising electrocatalyst for ORR. To validate the prediction we synthesize three different types of catalysts with various applied processes: (i) hydrothermally treated “Cu@N-C(hydro)”, (ii) “Cu@N-C(heat)” heat-treated at $T = 1000$ °C for 2 h, and (iii) “Cu@N-C(CO_2)” oxidized by CO_2 for 15 min at $T = 1000$ °C. It is shown that applying the CO_2 treatment can be a key process controlling electronic structures and shell thickness of the materials leading the high ORR catalytic performance.

To alleviate the substantial overpotential problem in water splitting process storing the energy in fuels of O_2 and H_2 we develop hexagonal perovskite oxide with a transition metal of mixed oxidation states. Both computational prediction and experimental measurements consistently show that its performance is better than IrO2.



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Graphene/Sb_2O_4 nano-rod hybrid nanostructure for high-performance sodium-ion battery anode

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ABSTRACT—Sodium-ion battery (SIB) has attracted lots of interests recently, which was put forward to be a potential energy storage system for increasing green energy. Antimony-based materials have been attracted lots of interests as a promising candidate of its high theoretical capacity, including antimony and antimony oxides. However, the antimony oxide of Sb_2O_4 prepared through a chemical reaction process for SIB anode has attracted few attention. Herein, we adopted one-step simple process for Sb2O4@graphene by hydrothermal reaction I_2, $SbCl_3$ and graphene oxide. The hybrid nanostructure for sodium-ion battery anode has an excellent cyclability of 542.3 $mAhg^{-1}$ after 40 cycles and rate performance of 380 $mAhg^{-1}$ at a current density of 0.4 Ag^{-1}.

Validating a Central Approximation in Theories of Regular and Random Electrochemical Electrode Arrays

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Regular electrode arrays generally possess a symmetry, which (under certain conditions) allows to reduce their mathematical description to consideration of a single electrode of this array within the laterally bounded domain (known as 'unit cell' or 'diffusion domain') [1, 2]. In this case, by multiplying the simulated current of the single cell by the number of electrodes in the array one would obtain an electrochemical response of the whole array. The electrodes in arrays are generally ordered in hexagonal or square patterns, which result in hexagonal or square cross-sections of the unit cells, respectively. A straightforward approach to the mass-transport problem in such cells would require complex and time-consuming 3D simulations. Therefore, almost always an approximation is made in simulations by replacing the original cross-section with the circular one of the same surface area. At one hand, this greatly facilitates the simulations due to the possibility to formulate the mass-transport problem in two dimensions. On the other hand, although this approach was proven to be effective in practice, the error introduced by this approximation, to the best of our knowledge, was never been studied or even estimated. Knowledge of this error, however, is extremely important since it affects the accuracy of the quantitative information (rate constants, diffusion coefficients etc.) extracted from the fitting of the experimental and simulation data.

For this reason, we performed 3D Brownian motion simulations in single cells with circular, square and hexagonal cross-sections in systems with inlaid, recessed and protruding electrodes. It was found that for the experimentally interesting range of system geometries the approximation gave rise to an experimentally indistinguishable error (less than 5%) in all aforementioned situations [2].

The same methodology was used to assess and revisit the simulation approaches for the randomly distributed electrode arrays. The obtained results provide a better understanding of random arrays behaviour as well as validate substitution of the Voronoi cells (unit cell around an electrode in a random array) by the circular unit cells in simulations with a reasonable accuracy (error less than 10%). Finally, an easy to compute analytical approximation was proposed for the response of the random electrode array for an arbitrary distribution of the electrodes.

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Co-electrodeposited Mn_2O_3-Au Composite Spherical Network: Formation mechanism, Electrocatalytic and Charge storage properties

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In this work, we have incorporated gold nanostructures within manganese oxide matrix by one step co-electrodeposition technique using cyclic voltammetry. A thorough comparative study between the pristine oxide and the composite material has been performed in terms of their morphologies, structure, and electrochemical properties. An interesting feature is the distinct difference of morphology of the composite, which was investigated in detail by microscopy (SEM, TEM) and electrochemical analyses, based on which a probable formation mechanism has been proposed. Both the pristine as well as the composite material have been extensively characterised using x-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS). The as obtained Mn_2O_3-Au composite modified ITO (Indium tin oxide coated glass) electrode shows reduced interfacial charge transfer resistance, improved electro-catalytic and charge storage properties. Improved hydrogen peroxide oxidation as seen from cyclic voltammetry and chronoamperometery studies and and increased charge carrier density as estimated from the Mott-Schottky analyses suggest the Mn_2O_3-Au modified ITO working electrode may find useful electrochemical applications in fields of electrocatalysis and charge storage devices.

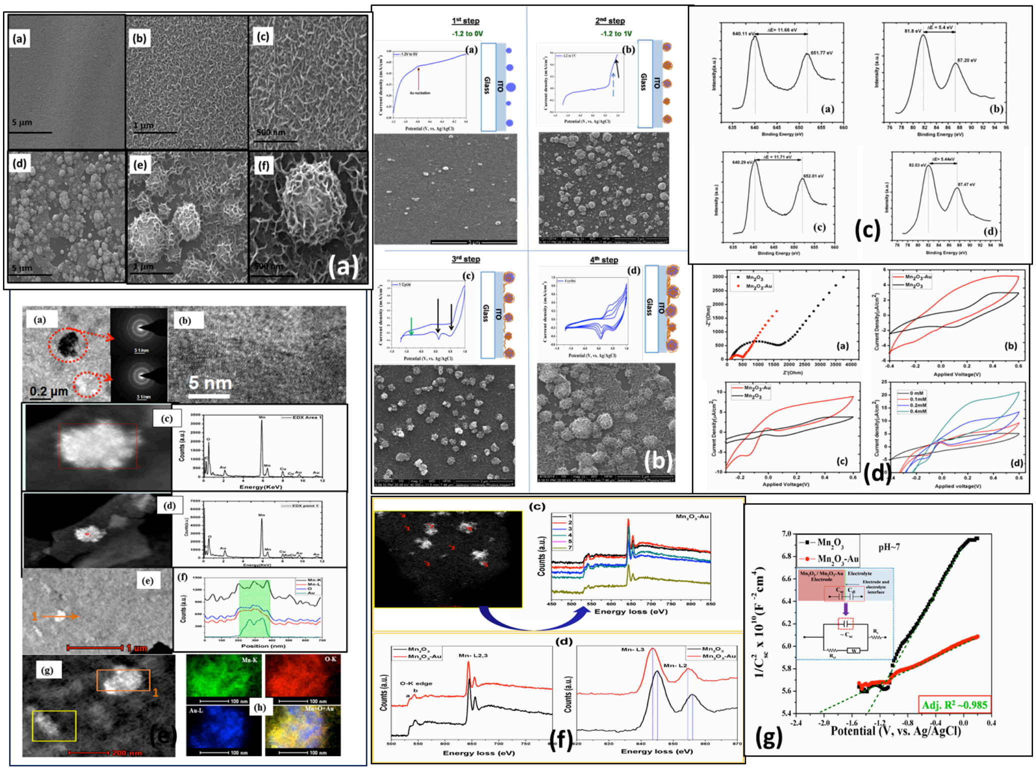

Figure1: comparative SEM images of Mn_2O_3 mat and Mn_2O_3-Au composite microsphere (a), formation mechanism of composite microsphere (b), XPS spectra of pristine and composite samples (c), electrochemical characterizations of Mn_2O_3-Au composite sample (d), detailed TEM study of Mn_2O_3-Au composite (e), EELS study of Mn_2O_3-Au composite (f), Mott-Schottky analyses (g)

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Effect of Carbon Monoxide Poisoning on Bi-Layered Anode Catalyst Layer of PEMFC

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We develop a one-dimensional, steady sate bi-layered anode catalyst layer model to simulate the carbon monoxide poisoning effect on PEMFC. The catalyst sub-layer (type A) near gas diffusion layer is capable to adsorb and react with CO; while the sub-layer (type B) near the membrane serves as the major portion for the oxidation of hydrogen. Proper combination of the bi-layer thickness enhances the performance of catalyst layer in the presence of carbon monoxide. Fig. 1 plots the current densities predicted by the model at various combinations of type A + type B. The hydrogen feed percentage is fixed at 75%, while the carbon monoxide concentrations are 10, 30, and 100 ppm, respectively. It is clear that optimum combination of the two sub-layers can be found using this model.

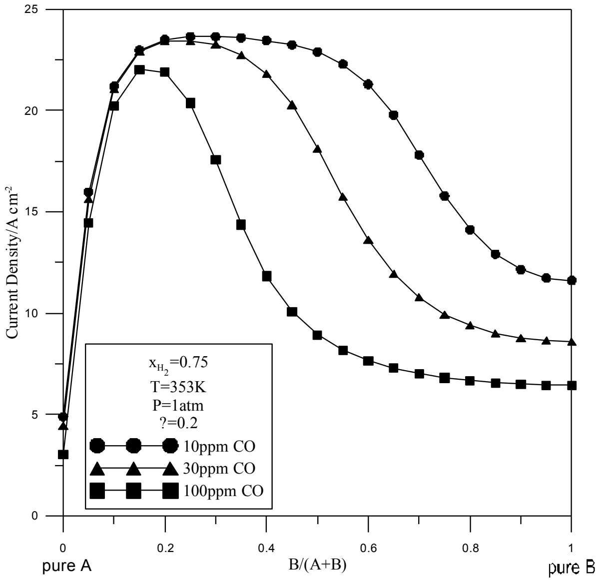

Fig. 1. Anode current densities as a function of combination on type A and type B sub-layers.

Ultra-sensitive detection for tryptophan based-on β-cyclodextrin conjugated magnetic graphene oxide modified glassy carbon electrode

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An ultra-sensitive and selective sensing platform was fabricated for detection of tryptophan (Try) based on β-cyclodextrin functionalized magnetic graphene oxide (MGO-CD) nanocomposites. The MGO-CD was prepared by a layer-by-layer assemblied method and characterized by fourier transform infrared (FTIR), transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and zeta potential. The electrocatalytic oxidation and detection of tryptophan (Try) based on nanocomposites-modified glassy carbon electrodes (GCE) were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The MGO-CD exhibited extraordinary electrochemical response towards the oxidation reaction of Try. The current response of Try at the modified electrode showed an excellent analytical property. The results confirmed that the synergistic effect between MGO and β-CD could distinctly improve the selectivity and reduce the detection limit for Try electrochemical sensing. The sensitivity and selectivity were greatly improved due to the conjugation of β-cyclodextrin (β-CD). The analytical detection of Try in amino acid pharmaceutical preparations obtained favourable results. The proposed method was sensitive and precise for the determination of Try. This new type of strategy may provide potential applications for the clinic application.

A B

Fig.1 (A) Preparation of MGO-CD and the MGO-CD/GCE. (B) Nyquist plots of EIS at bare GCE (a), MGO/GCE (b) and MGO-CD/GCE (c) in 5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution containing 0.1 M KCl at a bias potential of 0.23 V.

Fig. 2 Cyclic voltammograms (CVs) of bare GCE (a), MGO/GCE (b) and MGO-CD/GCE (c) in 0.1 M PBS (pH 7.0) containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (A) or 1 mM tryptophan (B). Scan rate : 0.1 V/s.

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Electrochromic Properties of a Magenta Polypyrrole Derivatised with Methyl Red

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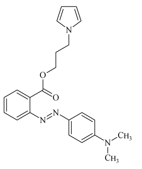
One of the major challenges in the area of molecular electronics is focused toward the synthesis of materials based on conjugated polymers with novel optoelectronic properties. Organic dyes have been used in different areas of science, such as medicine, physics, and chemistry, to produce chromatic changes or to investigate the effect of a light absorber specimen in well-known systems. Hybrid materials with colour-changing properties can be easily obtained by incorporating organic dyes, such as Indigo Carmin [1], Bromophenol Blue [2], Ramazol Black B and Dianix Red [3], to the polymer film. Fine-tuning and optimization of the conjugated polymer properties is achieved by modification of the polymer backbone or its pendant groups. In this work an electrochromic pyrrole derivative substituted with Methyl Red dye was prepared by a simple synthetic route and electropolymerised onto Indium Tin Oxide (ITO)/glass electrodes. The presence of the tertiary amine in the Methyl Red substituent of the monomer precursor (MRPy) prevents the electropolymerisation in usual systems such as tetrabutylammonium tetrafluoroborate ($TBABF_4$)/acetonitrile (CH_3CN) (Fig. 1). For this reason, 20 % boron trifluoride diethyl etherate (BFEE) was added to this system, to achieve electropolymerisation (Fig. 2). The behaviour of poly(MRPy) films upon doping and undoping was monitored by UV–vis-NIR spectroscopy in 0.1 mol L^{-1} $TBABF_4/CH_3CN$ (Fig. 3). Reversible changes in the colour occur for poly(MRPy) films from light magenta in the reduced state to dark magenta in the oxidised state. As the Methyl Red is a good pH indicator, the changes in the colour of the polymer films were also investigated in PBS buffer (pH = 2.0, 3.0, 5.0, 7.0 and 9.0), showing changes in the colour of the films from dark magenta in pH = 2.0 to yellow in pH = 9.0. These features make these materials potential candidates for application as active layers in optoelectronic devices and also as pH sensors.



MRPy

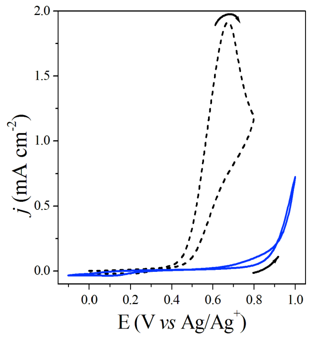


Fig. 1. CV of MRPy in $TBABF_4/CH_3CN$ (--) and in the same electrolyte with 20% BFEE (−), ν = 0.02 V s^{-1}.

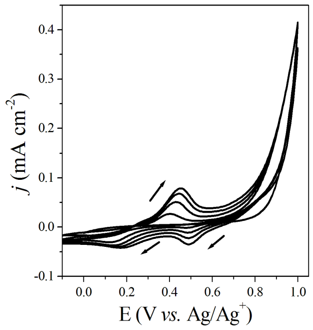


Fig. 2. CVs recorded during the electropolymerisation of MRPy in $TBABF_4/CH_3CN$ with 20% BFEE, ν = 0.02 V s^{-1}.

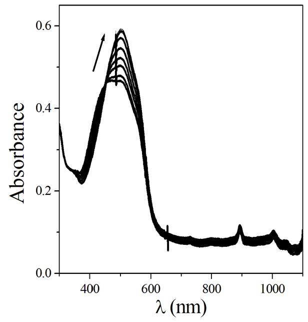


Fig. 3. Absorbance spectra of poly(MRPy) films deposited onto ITO in $TBABF_4/CH_3CN$ 0.1 mol L^{-1} as a function of the applied potential ($0.0 \leq E \leq 0.6$ V in 0.1 V intervals).

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Site-Specific vs. Non-Specific Wiring of Enzymes

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In recent years we were engaged with the problem of wiring enzymes and microorganisms to electrodes, in order to enable efficient electron-transfer between biological molecules and electrodes and to enable efficient biocatalytic transformations. Site-specific wiring was achieved by genetic code expansion tools, where a stop codon suppression approach was used to genetically encode for a specific site of attachment, where an unnatural amino acid may be inserted into a redox enzyme and could be used as an orthogonal chemical handle. The resulting modified E. coli cells were subsequently used in a biofuel cell and have shown good power out puts. In a different approach Graphene Oxide was used to encapsulate either genetically modified microorganisms such as yeast and E. coli, to demonstrate efficient coupling between those microorganisms and the electrode surface or modified enzymes that were used in similar matrices. In this case power outputs were even higher than with the site-specific wiring approach, presumably due to higher surface coverage. In addition, a unique technique was developed and studied to transduce bio-catalysis from surface displayed redox enzymes using the conductive tip of an AFM. By the site specific modification of bacterially surface displayed redox enzyme, we were able to pick up a single bacterium with the tip of an AFM and to follow the biocatalysis of ethanol with surface displayed alcohol dehydrogenase. These developments and unique site specific modification tools that were used in these studies will be discussed.

Poly(acrylic acid)–based Hybrid Inorganic–Organic Electrolytes for Electrical Double Layer Capacitors Application

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Abstract:

Nanocomposite polymer electrolytes (NCPEs) based on poly(acrylic acid)(PAA) and titania (TiO_2) are prepared by solution casting technique. The ionic conductivity of NCPEs increases with the weight ratio of TiO_2.The highest ionic conductivity of $(8.36\pm0.01)\times10^{-4}$ Scm^{-1} is obtained with addition of 6 wt.% of TiO_2 at ambient temperature. The complexation between PAA, LiTFSI and TiO_2 is discussed in Attenuated Total Reflectance–Fourier Transform Infrared (ATR–FTIR) studies. Electrical Double Layer Capacitors (EDLCs) is fabricated using the most conducting NCPE and carbon–based electrodes. The electrochemical performances of fabricated EDLCs are studied through cyclic voltammetery (CV) and galvanostatic charge–discharge studies. EDLCs comprising of NCPE shows the specific capacitance of 28.56 F g^{-1} (or equivalent to 29.54 mF cm^{-2}) with excellent electrochemical stability.

Keywords: Poly(acrylic acid); TiO_2; Nanocomposite polymer electrolytes; EDLCs; Capacitance

TiO_2 modified Cu cathodes for electrocatalytic CO_2 reduction

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Efficient conversion of CO_2 into liquid fuels has the potential to "revolutionise green energy technologies" [1]. CO_2 can be converted to methanol by electrochemical reduction, although there are significant challenges that must be overcome before this technology is economically viable [2]. In particular, "no material is known to catalyse the electroreduction of CO_2 to fuels both efficiently and selectively" [3]. We propose that the key to increasing the activity of electrocatalysts for CO_2 reduction lies in exploiting the interface between metallic and oxide phases. This is supported by the growing evidence that suggests that these interfaces provide much of the activity in both heterogeneous and electro- catalysis [4-7].

In our case, we have been concentrating on studying the influence of the Cu-TiO_2 interface on the product selectivity and energy efficiency using Cu surfaces modified with either TiO_2 nanoparticles or layers. In particular, we are interested in understanding why Cu based catalysts are highly selective for methanol formation from gas-phase CO_2 reduction, whereas the electrochemical reduction of CO_2 on metallic Cu almost exclusively results in the formation of hydrocarbons other than methanol. As methanol formation has been observed on Cu oxide cathodes [8-10], it seems that oxide sites facilitate methanol formation due to the stabilisation of the methoxy intermediate [11]. However, as Cu oxides are be reduced to metallic Cu under the strongly reducing conditions of CO_2 reduction, our goal is to instead utilise Cu-TiO_2 interface to stabilise of the methoxy intermediate and produce methanol.

In this paper we will discuss the product selectively of electrochemical reduction of CO_2 on TiO_2 nanoparticle coated Cu cathodes as analysed by online gas chromatography and post electrolysis HPLC. In general, we find that TiO_2 additions can reduce the overpotential of CO_2 reduction but this has the effect of also influencing the product selectivity. These results are compared to CO_2 reduction on the native oxide film on Ti cathodes to provide evidence of the possible synergetic effects due to the TiO_2-Cu interface. While the initial results appear promising, these electrodes can be deactivated and appear to be very sensitive to trace impurities in the electrolyte. We also will discuss the influence of mass transport on the product selectivity as this can be altered at cathodes modified by layers of nanoparticles.

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Electrochemical codeposition of cobalt and ruthenium from acidic chloride electrolytes

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Co-Ru/Ru alternate nanostructures exhibit giant magnetoresistance (GMR). Enormous research effort is turned toward low-cost and simple preparation methods of materials, which display GMR. Generally Co-Ru alloys are obtained by physical (PVD) or chemical (CVD) vapor deposition techniques [1]. Electrodeposition of pure Ru as well as Ru containing alloys is quite complex process. The redox potentials of Ru are: 0.25 V and 0.46 V vs SHE for $Ru^{3+(aq)}/Ru^{2+(aq)}$ and $Ru^{2+(aq)}/Ru^{(s)}$, whereas of Co in acidic solution: + 1.81 V and – 0.28 V vs SHE for $Co^{3+(aq)}/Co^{2+(aq)}$ and $Co^{2+(aq)}/Co^{(s)}$, respectively [2]. The Co-Ru alloys deposited from sulphate-sulphamate electrolytes were reported by Juzikis *et al.* [3, 4]. In the work of Laszlo *et al.* one can find an information concerning co-deposition of Co with Ru from chloride-sulfate bath [5]. In this work chloride complexes were used for the first time for Ru-Co codeposition.

The work describes the mechanism responsible for formation of Co-Ru alloys through electroreduction of aquachloro complexes of Co(II) and Ru(III) in an aqueous acidic chloride electrolyte of pH = 3. Identification of electrode reactions was performed based on voltammetric and electrogravimetric tests. Potential range for alloy deposition and current efficiency of electrolysis were deteremined by EQCM and voltammetric tests, respectively. UV-Vis spectrometry was used to examine electrolyte stability. The influence of concentration of various forms of Co(II) and Ru(III) complexes $\Sigma[CoCl_x(H_2O)_{6-x}]^{2-x}$ (x = 0, 1, 2) (10 – 100 mM), $\Sigma[RuCl_y(H_2O)_{6-y}]^{2-y}$ (10 mM) as well as applied potential (from – 0.5 to – 0.9 V vs Ag/AgCl electrode), pH of electrolyte (1 – 3) and temperature range (25 – 70 °C) were examined towards composition, structure and morphology of deposited Co-Ru alloys. The performed structural analysis showed a high influence of the synthesis conditions on the structure and morphology of the obtained alloys.

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Molecular Rectification and Electron Transport in “Highly” Modified Electrodes

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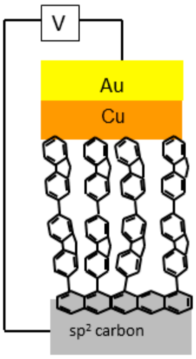
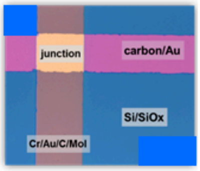
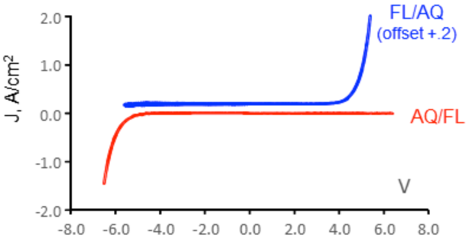
Carbon-based modified electrodes are widely used for practical analysis, notably in home glucose sensors which use screen-printed carbon substrates. A modified electrode also represents a direct electronic connection between a carbon surface and thin layers of molecules, and permit introduction of a wide variety of chemical recognition or catalytic events on a conducting surface. We make solid-state electronic devices on sp^2 hybridized graphitic carbon surfaces modified covalently with organic films with thicknesses of 1- 25 nm. Direct electronic contact is provided by vapor deposition of a conducting top contact, which may itself be made of graphitic carbon. Electron transport is such “molecular junctions” depends on the molecular layer structure and thickness, and is often controlled by quantum mechanical tunneling for thin (<5 nm) layers. The current discussion deals with molecular layers greater than 5 nm thick, with the main question being “how to electrons traverse distances too great for tunneling, and how is such transport affected by molecular structure?” Valuable insights addressing this question are provided by two experiments: rectification in molecular bilayers and light emission from molecular junctions.







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The importance of the Hofmeister series on the ability of ions and water to penetrate through self-assembled monolayers; Implications for device fabrication on Si(100) surfaces.

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The employment of Si(100) on devices dedicated to work into aqueous environments (e.g. sensors, biosensors and biologically active surfaces) may present at least three important commercial advantages over similar systems in which metallic based platforms are applied: (i) Si(100) already present a well-established technology for low-cost bulk production; (ii) high-purity single-crystal Si(100) wafers are easier available in large scale; (iii) electronic properties of Si(100) can be tuned according to dopant type and/or concentration.[1] The utilization of semiconductors at this field also opens perspective for aqueous based electrochemical (bio) sensors rival with optical devices on matching the density of sensing elements in an array. This is possible because electrochemistry can be confined in semiconductors at micrometer scale on any spot by shining a radiation with energy above the bandgap, so an array can be formed by driving the radiation at different positions of the semiconductor. An important example in this field is the light-addressable potentiometric sensors (LAPS), which use AC photocurrents to detect changes in the capacitance of the semiconductor depletion layer, making possible LAPS sense changes of pH, redox potential and ions concentration in aqueous solutions. However, LAPS remain as chemical sensors with no DC currents crossing the interface. One of the main challenges for achieving a faradaic Si(100)-based sensor consists on avoiding the growth of the insulator SiO_x layer when the surface is electrochemically applied in aqueous electrolytes. Our group has recently reported a solution capable of working as a game turning at this field. It consists of a combination of surface chemistry that prevents oxidation of Si(100) by protecting it with a 1,8-nonadiyne based self-assembled monolayer (SAM) that is still sufficiently thin for allowing electron transfer through it, so electrochemical information can be either read from or written onto these surfaces using light.[2]

As an example, light-activated DC currents were efficiently monitored in 1.0 M $HClO_4$ using click-chemistry attached ferrocene, with no SiO_x growth after 1000 electrochemical cycles. The present work aims to expand the understanding of how different electrolytes can affect the protection of Si(100), as different light-activated sensors may be required to operate in very different electrochemical matrices. The strategy consisted of employing different salts of the Hofmeister series as electrolytes. Consequently, we aim to correlate the effect of the presence of kosmotropic ions (strongly hydrated) and chaotropic ions (weakly hydrated) with the breakdown of the SAM at different electrochemical potentials. The techniques employed for monitoring the SiO_x formation at macroscopic and microscopic levels consisted on contact angle and X-ray photoelectron spectroscopy (XPS). The first one allows the observation of the spread of an electrolyte droplet while a potential is applied to the protected Si(100) and the XPS allows the observation of the surface before and after electrochemical tests with the different electrolytes, providing the quantification of SiO_x growth in each situation. The observed results allowed us to affirm that: (i) strongly hydrated SO_4^{2-} based electrolytes are more prominent to forming SiO_x, independently if the correlated cations are chaothropic or kosmotropic; (ii) at anodic scans, weakly hydrated ClO_4^- based electrolytes only form SiO_x before 1V if a kosmotropic cation is present. If not, significant SiO_x formation is only achieved after this potential; (iii) at cathodic scans, weakly hydrated ClO_4^- based electrolytes does not form significant amount of SiO_x, independently if the correlated cations is chaothropic or kosmotropic; (iv) Cl^- based electrolytes are located in the middle of Hofmeister series and presented a behavior between kosmotropic SO_4^{2-} and caotropic ClO_4^- for SiO_x formation, which gives us some confidence to predict the effect of the ions considering the binding force with water.

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Electrochemically Induced Deposition of Enamel-Like Coating for Tooth Repair

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INTRODUCTION: Dental caries is one of the common chronic diseases in the world. Increasing attention is paid to the restoration of the initial enamel lesions in order to prevent deep caries lesions. In this abstract, a mild electrochemical process was used to produce synthetic enamel coating on tooth surface for early caries lesions repair.

MATERIALS AND METHODS: Fresh human third molars extracted without visible evidence of caries were used in this investigation. The enamel surfaces of the specimens were firstly treated with an acid solution for 1 minute, subsequently immersed into an electrolyte that mainly contained $Ca(NO_3)_2$, $NH_4H_2PO_4$ and $NaNO_3$. The pH value of the electrolyte was adjusted to 7.0 by NaOH solution. A platinum plate was served as counter electrode and a slice of stainless steel as working electrode. Each specimen was put entirely close to the stainless steel, and the enamel surface subjected to coating faced to the counter electrode. The electrodeposition was performed for 0.5~2h with the current density of 0.2~1.0 mA/cm^2 under 30~55□. The microstructure and morphology of the coating were characterized using XRD, SEM, TEM and EDX. The hardness and contact angle of the surfaces of the specimens was determined using a Vickers microhardness tester and a contact angle analyzer, respectively. A Pt-Ir microsensor was used to *in situ* evaluate the pH values at the enamel/ electrolyte interface.

RESULTS: Several kinds of nanostructure patterns were produced on the surface of enamel under different experimental condition. As overall pH values at the enamel/solution interface were higher than 7.64, HA coating with acicular morphology was formed after 1h treatment of electrochemistry. XRD and EDX analysis revealed that the coating consisted of hydroxyapatite (HA) crystals ($Ca/P \approx 1.67$) and had the (002) preferred orientation. SEM and TEM observation showed that the coating, 1μm to 10μm in thickness, bonded to the enamel tightly. In addition, HRTEM observation substantiated that the HA coating preferentially grew along the orientation of the HA crystal of the enamel prism. The contact angle values ranged from 136.4° ± 10.18° to 160.4° ± 6.79° after formation of coating, significantly higher than those of intact enamel ($P<0.001$), which suggested that the antibacterial activities of the enamel were improved after formation of coating. Moreover, the hardness of the coating (282.64 ± 16.66 VHN) approximated to that of the healthy enamel (318.76 ± 13.83 VHN). pH measurement at the substrate/solution interface showed that as soon as the experiment began, pH increased immediately and reached to 7.64. During the process of the experiment, pH increased to 7.98 by 40 min, and then decreased slowly to 7.91 when the experiment ended.

Study of Gold Electroplating by Constant and Pulse Current Method with Non-Cyanide Gold Sulfite Electrolyte

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Gold has been applied as movable structures for micro-electro-mechanical systems (MEMS) devices. Yamane et al. suggested MEMS accelerometers made of gold, a high density (19.30 g/cm^3) material, could give a much higher sensitivity than that of silicon [1,2]. Electrodeposition is one of the commonly used methods for fabrication of the micro-components used in MEMS [3]. Properties of the electroplated gold and the applications in MEMS devices are highly dependent on the type of the electrolyte and the electroplating method used. For example, the reliability of the components used in MEMS is highly dependent on the mechanical properties, especially when size of the components is decreased to micro-scale for applications in MEMS. Thus, clarifying the micro-mechanical properties, such as young's modulus and yield strength, of the gold materials electroplated with different electrolyte and electroplating method is important for the applications of electroplated gold in MEMS. In this study, micro-compression tests of micro-specimens made of three types of electroplated gold will be evaluated, which are constant current electroplating (CE) with cyanide-based electrolyte (CE-Cy), CE with sulfite-based electrolyte (CE-S), and pulse current electroplating (PE) with sulfite-based electrolyte (PE-S).

The cyanide-based and sulfite-based gold electrolytes used in this study were both commercially available gold electrolyte provided by Matex Japan Co. Ltd. The cyanide-based electrolyte contained 20 g/L of gold and pH of 5.0. The current density used for the CE-Cy was 4 mA cm^{-2}. The sulfite-based electrolyte contained 10 g/L of gold and pH of 8.0. Cu plate and Pt plate were used as the cathode and anode, respectively. The current density and average current density for the CE-S and PE-S were both 5 mA/cm^2. For the PE-S, the on-time current density (I_{on}) was 10 mA/cm^2, and the off-time current density (I_{off}) is 0 mA/cm^2. On-time (T_{on}) and off-time (T_{off}) of the PE-S were both 10 ms. The reaction temperature was kept at 60 ºC for all of the electroplating processes.

Micro-pillars made from the gold films were fabricated by focus ion beam (FIB) milling. Details of the fabrication methods can be found in previous studies [4-6]. Size of the fabricated pillars was 10 μm×10 μm×20 μm. The long side of the pillar was parallel to the substrate/gold interface. The micro-compression tests were carried out using a test machine specially designed for micro-sized specimens equipped with a flat-ended diamond indenter at a constant displacement of 0.1 μm/s controlled by a piezo-electric actuator.

All of the three gold films had grain size in nano-order, and therefore, have higher strengths than that of bulk gold materials. The grain size was estimated from X-ray diffraction patterns and the Scherrer equation. The CE-Cy gold film had grain size of 22.8 nm and showed inhomogeneous structure under scanning electron microscope (SEM) observation. The CE-S specimen showed textures along the film growth direction and grain size of 17.5 nm. The PE-S specimen showed homogeneous structure with no obvious grain/texture boundary and grain size of 10.4 nm. In the compression test, the CE-S and PE-S pillars showed ductile deformation, and brittle fracture was observed for the PE-S pillar.

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Holey graphene/PPy nanoparticle aerogels with three-dimensional hierarchical structure for high performance supercapacitor

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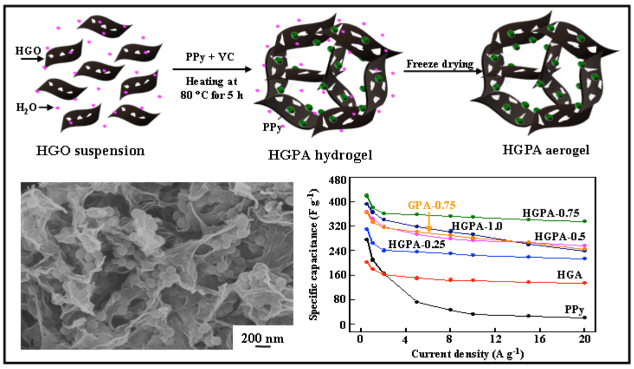
Supercapacitor is an important class of energy storage devices, and its capacitance is mainly influenced by the electrode material[1]. Polypyrrole (PPy) is a promising electrode candidate, but its application for PPy-based electrodes is seriously limited due to their low rate capability and poor cycling stability. Therefore, it becomes more and more urgent to overcome the inherent defect of PPy-based electrodes and improve their capacitive performance in energy storage[2]. The holey graphene (HG) nanosheets possesses higher surface area and much more active sites and edges for the ion diffusion shortcuts between different layers of graphene, thus it may be improve the capacitance retention of PPy/graphene hybrid electrodes by using HG nanosheets and PPy nanoparticles as the constructing units.

In the present work, holey graphene/polypyrrole hybrid aerogels (HGPAs) were fabricated by freeze-drying HG/PPy hydrogels, which were assembled by using HGO nanosheets and PPy nanoparticles as the assembling primitives. The as-prepared HGPAs showed an interconnected and stable 3D hierarchical porous network, and PPy nanoparticles were uniformly embedded in the aerogel. The unique hierarchical porous structure and synergistic effect between PPy nanoparticles and HG nanosheets made HGPA hybrid aerogel electrode with a mass ratio of PPy/HGO=0.75 exhibited high specific capacitance (418 F g^{-1}) at a current density of 0.5 A g^{-1}, extremely outstanding rate capability (80%) at various current densities from 0.5 to 20 A g^{-1} and good cycling performance (74%) after 2000 cycles in 1.0 M KOH aqueous electrolyte. Moreover, the effect of the PPy nanoparticle sizes in HGPAs on their electrochemical properties indicated that PPy nanoparticles with relatively larger sizes were favorable of the good capacitive performance for the obtained electrodes. The facile and efficient preparation method for HGPAs electrodes may be developed for preparing other holey graphene-based hybrid aerogels with structure-controllable nanostructures.



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Novel Surface Modification of Graphite with Excellent Performance for Lithium-ion Battery

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Research in exploring alternative high-capacity lithium-ion battery (LIB) anodes in the past decades has predominantly focused on Li-alloying and conversion-reaction anodes. In spite of their potential high capacities, ranging from > 3000 mAh g^{-1} for Si anode to slight higher than 500 mAh g^{-1} for most metal-oxide conversion anodes, lithiation of these anodes involves formation of low-density lithiated products, resulting in tremendous volume expansion. The cyclic dimensional variations during charging-discharging cycles is known to result in pulverization of active-material particles and cracking and crumbling of electrode structure, leading to fast capacity fading and poor cycle life. On the contrary, graphite has an excellent cycle stability based on its theoretical lithiation capacity of 372 mAh g^{-1} with the potential plateau taking place well below 0.2 V (versus Li/Li^+). Composite anodes, therefore, comprising a limited amount of the alloying anodes, such as Si, to enhance the capacities of the graphite (G) anodes have been considered as attractive transient products for advanced high-energy LIBs before fully alloying anodes can be realized. In this paper, we report for the first time the use of thiophene-based conducting polymer blend, namely PEDOT-PSS, as a "capacity-amplifier" of several graphite-based anodes. PEDOT-PSS can be easily coated on the graphite surface by a conventional mixing-and-drying process and the electrode exhibits enhancing capacity (> 700 mAh g^{-1}) and good cycle stability (> 600 mAh g^{-1} after 300 cycles at 50 ^{o}C) without suffering from the volume expansion-induced capacity fading problem.

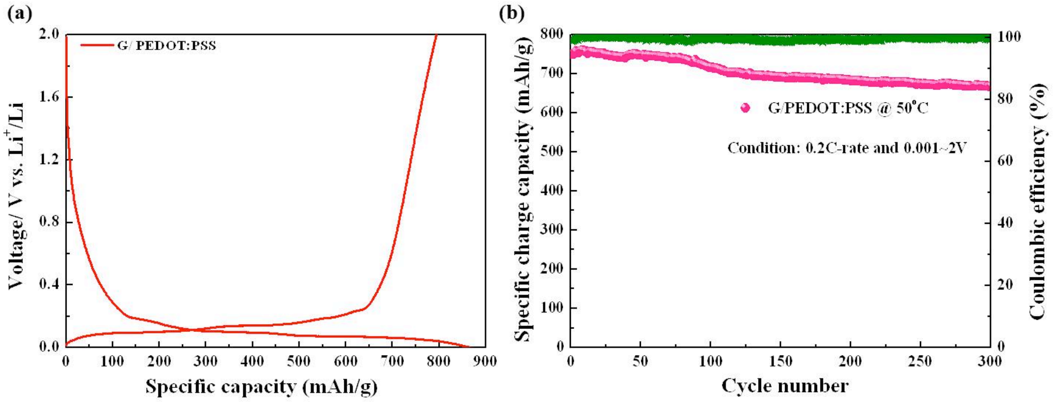

Figure 1(a) the second cycle charge–discharge voltage plots of G/ PEDOTPSS electrode acquired at 0.1 C-rate; (b) specific capacity versus cycle number of G/ PEDOTPSS electrode at a current density of 0.2 C-rate at 50 ^{o}C.

Preparation and Characterization of Gold Films by Electroplating with Supercritical Carbon Dioxide

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In recently years, gold materials have attracted much attention and are commonly used in micro-electrical-mechanical systems (MEMS) devices (i.e., capacitive accelerometer [1]) due to their high chemical stability, corrosion resistance, electrical conductivity, and density [2]. Among the deposition methods, electroplating (EP) is one of the commonly used methods for preparation of the metal films, which the morphology, crystal structure, and deposition rate could be easily controlled by varying the EP parameters [3]. On the other hand, application of supercritical carbon dioxide ($scCO_2$) in the EP process was proposed to be effective to overcome the problems encountered in conventional (CONV) EP of miniaturized components [4, 5], which surface tension of water and evolution of hydrogen are found to be the major causes of the defects. $ScCO_2$ is CO_2 at temperature and pressure above its critical point (31.1°C and 7.38 MPa). $ScCO_2$ has extremely low surface tension and is non-polar, which can promote transfer of materials into confined space and removal of H_2 gas bubbles away from the cathode. Surface smoothness of the nickel and copper films electroplated with the $scCO_2$ contained electrolyte (SCE) was found to be improved, and complete filling of copper in to nanovias having 70 nm in diameter and 350 nm in depth was obtained by EP with the SCE (EP-SCE). In addition, grain refinement effect was often observed for the metal films prepared by EP-SCE, which then leads to an enhancement in the mechanical strength because of Hall-Petch relationship [6]. With the advantages of the SCE, it is expected that performance of the electronic devices could be further improved using the gold films fabricated by the EP-SCE.

The gold electrolyte used in this work was commercially available non-cyanide sulfite-based electrolyte, which contains 10 g/L of gold and pH of 8.0. For the EP-SCE, 20 vol.% of CO_2 with respect to the overall volume of the reaction chamber and the temperature at 40°C were used. The pressure was varied from 5 to 15 MPa. The current density used was 5.0 mA/cm^2. Properties of the electroplated gold films were evaluated by a digital optical microscope, scanning electron microscope, X-ray diffraction (XRD), and atomic force microscope.

Using the EP-SCE, bright gold films were obtained. Grain sizes of the gold films fabricated by CONV EP with the same electrolyte and the EP-SCE were 22.8 and 13.6 nm, respectively. Grain size of the gold films was estimated by Scherrer equation and the XRD patterns. This result indicated that the grain refinement effect could be also attained in gold EP-SCE.

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Pulse Electroplating of Ultra-Fine Grained Au Films with High Strength for Micro-Electrical-Mechanical System Devices

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Au is the most commonly used as contact material for high reliability electrical connectors, circuit boards, and as functional component for micro-electrical-mechanical system (MEMS) devices [1,2]. Electroplating has been applied extensively in fabrication of Au films used for all kinds of devices. Among the electroplating techniques, pulse electroplating is a technique known to control the properties of the deposited films by regulating the pulse amplitude and width. Therefore, morphology, crystal structure and deposition rate of the Au films can be controlled precisely [3].

In this work, grain refinement and surface smoothening of Au films were achieved by pulse electroplating using non-toxic sulfite-based electrolyte. Micrographs obtained by atomic force microscopy (AFM) and X-ray diffraction (XRD) patterns indicate that the surface of the pulse electroplated Au films possess less defect, lower surface roughness, smaller grain size, and denser texture when compared with the Au films prepared by conventional constant-current electroplating. By XRD analysis and Scherrer equation, the estimated grain size of the Au film prepared by pulse electroplating was 10.5 nm, and was much smaller than the grain size of the Au film prepared by constant-current electroplating, which was 22.8 nm. The grain size achieved by the pulse electroplating is even smaller than previous reports [3-5]. This can be attributed to the higher pulse current density which leads to an increase in the nucleation rate during the on-time period.

Mechanical strength in micro-scale of the Au films was also evaluated to determine the reliability and lifetime of the components composed of the electroplated Au. After the electroplating, micro-pillars made from the Au films were fabricated by focus ion beam (FIB) milling. Size of the fabricated pillar was fixed at 10 μm ×10 μm×20 μm. The micro-compression test was carried out using a test machine specially designed for micro-sized specimens developed in our laboratory. The pulse electroplated Au micro-pillar acquired a large increase in the compressive strength from 600 to 800 MPa when the grain size approaches the nanoscale, which the grain size was close to 10.4 nm, presumably due to the grain-boundary strengthening known as the Hall-Petch effect [6]. This strength is much higher than that of bulk Au materials, which is only 55~200 MPa. The strength is even higher than that of the micro-pillar fabricated from the constant-current electroplated Au films. These results reveal that the pulse electroplated Au micro-pillar possesses better ductility and malleability than that fabricated by constant-current electroplating and demonstrate that pulse electroplating is a promising technique to fabricated Au functional micro-components especially for the advanced MEMS devices.

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Voltammetric and Simulation Analysis into the Determination of Acetaminophen using Multi-walled Carbon Nanotubes Dispersed in Polyethylenimine

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Acetaminophen (ACOP) is an antipyretic and analgesic drug used for the relief of pain associated with neuralgia, cancer pain and headache. Meantime a chronic use or large dosages could cause liver disorders, nephrotoxicity and inflammation of the pancreas. Thus, it is imperative to develop simple, fast and accurate methodology for ACOP determination. Due to its electroactive groups of hydroxyl and acetamido in benzene ring, ACOP can be detected by the electrochemical methods. The aim of this work was to develop a sensor using a glassy carbon electrode (GCE) surface modified with the dispersion of functionalized (acid medium for 4h) multi-walled carbon nanotubes (*f*MWCNT) in the presence of polyethylenimine (PEI) for ACOP determination. It was used Ag/AgCl/Cl^-_{sat}, platinum and GCE/PEI-*f*MWCNT surface as reference, auxiliary and working electrode, respectively. Experimental conditions such as pH and square-wave voltammetry parameters were optimized. The electrochemical behaviour of GCE/PEI-*f*MWCNT was recorded in BR buffer pH 5 in the presence at 1.96×10^{-4} mol L^{-1} ACOP and exhibited a pair of well-defined redox processes, suggesting that the reversibility of ACOP is significantly improved in comparison to irreversible oxidation peak on bare GCE. The redox process is controlled by adsorption and the number of the transferred electrons, charge-transfer coefficient and the value of apparent rate constant were evaluated to be approximately equal 2, 0.5 and 0.50 s^{-1}, respectively. Simulations studies for ACOP and its oxidation products were performed by means of density functional theory (DFT). Molecules were fully optimized using B3LYP functional and 6-311+G(d) basis set. It was evaluated the interaction between ACOP and *f*MWCNT in the absence and in the presence of PEI. First, the minimum energy was obtained when the ACOP adsorbed on the internal surface of the *f*MWCNT. Secondly, in the presence of PEI, the ACOP adsorption was stronger about than 10 kJ mol^{-1} and occurred on external surface of *f*MWCNT nearby a PEI dimer. The position of the ACOP molecule over the surface in both cases was very similar, about 4 Å of distance, and the aromatic ring lay over the *f*MWCNT. The analytical curves were obtained for concentrations of ACOP ranging from 9.99×10^{-8} to 6.95×10^{-6} mol L^{-1} (r = 0.9953). The calculated values limit of detection and quantification were 5.12×10^{-8} mol L^{-1} and 1.71×10^{-7} mol L^{-1}, respectively. The different spiking levels were tested in Tylenol®500 mg and Tylenol®DC samples. Table 1 shows the recovery data for this methodology.

Table 1. Values of recovery and RSD percentages obtained by proposed methodology

	Tylenol®500 mg	Tylenol®DC
$[ACOP]_{added}$ (mol L^{-1})	9.9×10^{-7}	9.9×10^{-7}
$[ACOP]_{found}$ (mol L^{-1})	9.4×10^{-7}	1.1×10^{-6}
Confidence interval (%)	$\pm 2.92 \times 10^{-8}$	$\pm 3.3 \times 10^{-7}$
Recovery (%)	95.5	111.0
RSD (%)	1.2	5.1

The GCE/PEI-*f*MWCNT electrode demonstrated that the proposed procedure can be considered as an alternative for mechanistic studies and the determination of ACOP. In addition to presenting good sensitivity and analytical stability, this methodology also presents the great advantages of eliminating the interference from excipients from commercial formulations minimising the steps of preparation of the samples and also limiting the adsorptive problems related to the use of other solid surfaces.

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Functionalization of thermoplastique polyurethane nanopore with stimuli-responsive polymer brushes for advanced tuneable resistive pulse sensing

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Resistive sensing with nanopores has emerged in recent years as a versatile tool to measure and sense a range of species, including particles, molecules, ions, and biomolecules. Resistive pulse sensing is based on the fact that a particle passing through a pore, displacing conducting fluid within that pore, produces a transient increase in the pore's electrical resistance which in turn can be observed as a decrease in current. Concentration information can be gained from examining the current-pulse frequency, while particle characteristic information can be determined by investigating the current-pulse signature, e.g. average magnitude and duration of the current pulse. The surface properties of the particles and pore membrane, interactions of particles with pore wall surfaces and ion concentration, affect the sensor response.

In this project, we report for the first time, the functionalization of thermoplastic polyurethane nanopore's wall with stimuli-sensitive polymeric brushes that modulate the pore's properties upon collapse or expansion. We use Graftfast methode based on the reduction of diazonium salt to polymerise poly(acrylic acid) (PAA) or poly(hydroxyl ethyl methacrylate) (PHEMA) onto the walls of the nanopore. The coating was confirmed by the appearance of OH band on FTIR spectra of the coated pore. Contact angle of the PAA coated pores decrease from 101°±2 to 62°±3 after grafting indicating an increase in hydrophilicity. We also demonstrate the effect of the brushes on the interaction with the 'particles' passing through the pore and the resistive response. Negatively charged PAA brushes modulate the speed of the particle passing through the pore by significantly increasing osmosis force along the pore. Neutral HEMA brushes increase hydrophilicity of the pore, such coating can advoid non-specific adsoption of biomolecules on the pore's wall. We believe this research opens a wide range of possibilities for further pore functionalisation for dynamic sensing, studying interactions with various particulate systems (notably in biology), to control the dynamics of the particle transport through the pore.

Impact of Adsorption on Scanning Electrochemical Microscopy (SECM) Measurements and Implications for Nanoscale Geometries

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Scanning electrochemical microscopy (SECM) is an established electrochemical platform that enables the quantitative measurement of fast electron transfer (ET) kinetics, particularly, when coupled with modeling predictions from finite-element simulations. Nevertheless, the advent of nanoscale and nanogap electrode geometries that have an intrinsically high surface area-to-solution volume realizes the need for more vigorous data analysis procedures. In this situation, the adsorption of redox active species may have profound impact on the SECM electrochemical response, yet this has not been widely appreciated.

The oxidation of ferrocenylmethyl trimethylammonium, FcTMA$^+$ on highly oriented pyrolytic graphite (HOPG) is used to demonstrate the effects of reversible reactant adsorption within the semi-confined gap of the SECM geometry, a system which has recently received attention as one with apparently ultrafast kinetics.[1] Adsorption of the highly charged, FcTMA^{2+} species onto glass, which is often used to encapsulate ultramicroelectrodes employed in SECM, is also found to significantly affect the voltammetric tip response by participating in direct ET with FcTMA$^+$ species in solution.[2] We find that the combination of these two adsorption processes, the build-up of FcTMA$^+$ on the HOPG substrate surface and FcTMA^{2+} on glass surfaces provide additional contributions to the UME tip current response and consequently result in the incorrect assignment of tip-substrate heights, ET kinetics and thermodynamic parameters. The reduced surface area-to-solution volume ratio of nanogap experiments makes understanding the adsorption properties of the probe essential in order extract reliable kinetic data, especially if the electrode kinetics are fast.[3]

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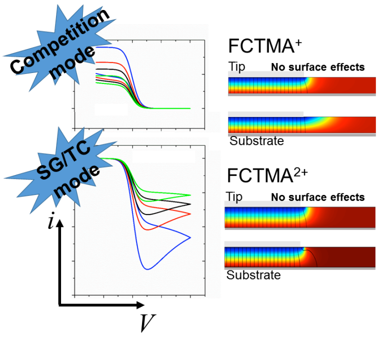

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Hydrometallurgical processing of sperrylite for platinum recovery

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ABSTRACT

Platinum Group Metals (PGMs) deposits are known for their scarcity, particularly outside of Southern Africa. Other than being precious metals, these metals are also essential industrial metals used in automobile catalysts, fuel cells, and a plethora of high technology applications. Direct leach approaches are being researched as smelting-based options are not suitable for smaller, lower grade and remote deposits. However, it has been found that one PGM mineral in particular, namely sperrylite, is highly refractory to most conventional leaching approaches. Sperrylite ($PtAs_2$) is a dominant Pt-bearing mineral in many PGM ores. Often sperrylite, together with other PGM minerals, are associated with chromitites, chalcopyrite and pentlandite.

To evaluate the potential of various leach alternatives, focussing specifically on sperrylite, high purity $PtAs_2$ crystals were exposed to lixiviant mediums and the electrochemical leach behaviour was studied. A series of linear sweep voltammetry were performed — using a rotating $PtAs_2$ disc working electrode — in the absence and presence of either ferric sulphate or hydrogen peroxide as oxidant or thiocyanate as complexing ligand. Strongly oxidizing conditions were not enough for achieving reasonable sperrylite leaching rates in sulphuric thiocyanate solutions. The dissolution rate of $PtAs_2$ in acidic thiocyanate solutions containing H_2O_2 was proposed to be surface controlled, owing to the effect of adhering reaction products, which act as an increased diffusion barrier to the transport of ionic and electronic species. However, alkaline leaching provided the most rapid dissolution of sperrylite, where AsO_4^{3-} was selectively leached over native Pt under oxidizing conditions.

Keywords: Hydrometallurgy, sperrylite ($PtAs_2$) leaching, thiocyanate, electrochemistry

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.

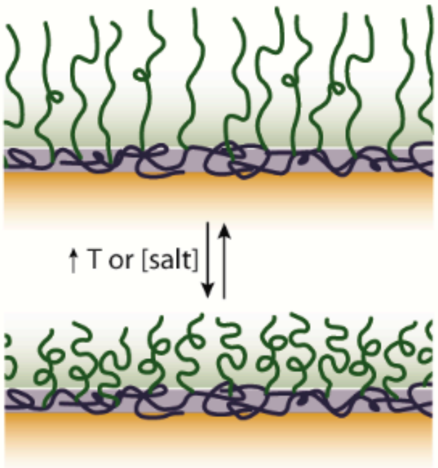

Figure: Salt or temperature-induced collapse of PPEGMMA brushes grafted on PEDOT, leading to a switch in surface properties.

Fabrication of MoO_3 Nanoparticles Modified TiO_2 Nanotube Films for Photocathodic Protection of Stainless Steel

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Photocathodic protection of metals by TiO_2 semiconductor materials has inviting prospects. However, TiO_2 can be induced only by ultraviolet light due to its intrinsic wide bandgap, and a high electron-hole recombination rate will reduce its photoelectric conversion efficiency, which limits its practical application. Therefore, the modification of TiO_2 semiconductor films is necessary to improve their photoelectrochemical properties. In this work, MoO_3 as a semiconductor with a narrower energy bandgap than that of TiO_2 was used to modify TiO_2 nanotube films for enhancing their photoelectrochemical performances.

TiO_2 nanotube array films were prepared on Ti foils by anodization at 20 V for 30 min in a two-electrode cell at room temperature. The Ti foil and a platinum sheet served as the working electrode and the counter electrode, respectively. The electrolyte used for the anodization was an aqueous glycerol solution with 0.5 wt% NH_4F. After the anodization, the specimens were annealed at 450 ^{o}C in air for 2 h. The MoO_3 nanoparticles on the prepared TiO_2 nanotube films were prepared by pulse current deposition in a two-electrode electrolytic cell consisting of the TiO_2 nanotube film specimen as the working electrode and a platinum sheet as the counter electrode. The electrolyte was a mixed aqueous solution containing $(NH_4)_6Mo_7O_{24}$ and Na_2MoO_4. Then the prepared composite film samples were annealed at 400 ^{o}C in air for 1 h. The films were characterized by scanning electron microscopy, X-ray diffraction, UV-visible spectroscopy and photoelectrochemical measurements.

The results indicated that the prepared TiO_2 film was composed of highly ordered nanotubes with an average inner diameter of about 100 nm and an average wall thickness of about 13 nm. The nanotubes were perpendicular to the Ti foil substrate and the nanotube length was about 1.3 μm. After the deposition of MoO_3 nanoparticles on the nanotube film, the film still retained the ordered nanotube appearance, but the inner diameter of the tubes decreased and the wall thickness increased.

The EDX spectrum of the prepared MoO_3/TiO_2 composite film showed the presence of Ti, O and Mo in the film. Furthermore, the XRD analysis indicated that the composite film was composed of anatase TiO_2 and orthorhombic α-MoO_3.

Compared with the pure TiO_2 nanotube film, the absorption edge of the MoO_3/TiO_2 composite film shifted to the longer wavelength region (400-650 nm), and the photoelectric conversion efficiency of the composite film was greatly improved.

The photocathodic protection effects of the prepared films as photoanodes were evaluated by measuring the potential-time curves of 403 stainless steel (403SS) in a 0.5 M NaCl solution coupled to the different films under dark and illumination conditions. The potential of the 403SS coupled to the pure TiO_2 film decreased by 440 mV under illumination. However, when the 403SS was coupled to the MoO_3/TiO_2 composite film, its potential decreased by 540 mV under the same illumination conditions, indicating that the composite film could provide a better photocathodic protection effect on the steel.

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Label-free electrochemical aptasensors for femtomolar detection of 17β-estradiol and potassium

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We report an electrochemical aptasensor for the rapid, label-free detection of 17β-estradiol (E2) from femtomolar to micromolar levels. The sensor features an aptamer-functionalised nanoporous conducting polymer electrode whose surface potential is probed via electrochemical impedance spectroscopy (EIS). The unprecedented detection limit towards E2 is explained *via* the redistribution of negative charges in the electrode double-layer region when the aptamer adopts a folded conformation around the small neutral target molecule, as shown in Fig. 1. The sensor responds approximately logarithmically over a wide dynamic range of E2 concentrations that spans biological trigger levels, with excellent discrimination against structurally similar molecules including progesterone, and robust operation in human urine. The generality of the approach of using conformationally gated small molecule binding aptamers is highlighted with a further example of potassium detection *via* the specific G-rich aptamer, which can also achieve fetomolar detection limit and excellent selectivity towards other ions. These instructions are an example of what a properly prepared meeting abstract should look like. Proper column and margin measurements are indicated.

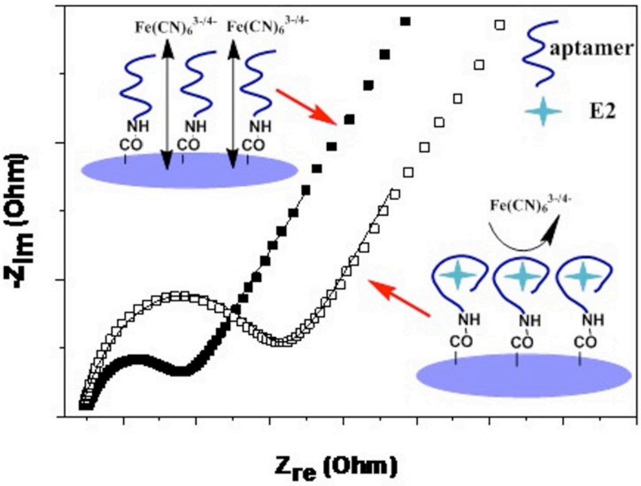

Fig. 1 EIS spectra, presented as Nyquist plots, of a P(Py-*co*-PAA)-aptamer modified electrode in phosphate-buffered saline solution with 5.0 mM $Fe(CN)_6^{3-/4-}$ before and after E2 detection.

Mechanical Characteristics of Structure Stability with Ti/Au Micro-Cantilevers Formed by Au Electroplating

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Gold materials are known to have excellent characteristics such as high chemical stability, corrosion resistance, electrical conductivity and density. These properties make gold as one of the promising materials for applications in micro-electro-mechanical systems (MEMS). MEMS accelerometers fabricated by gold materials are reported to have improved sensitivity compared to the conventional silicon-based design [1]. For fabrication of the MEMS devices, CMOS-MEMS (complementary metal-oxide-semiconductor-micro-electrical-mechanical system) technology has been developed to improve performance of the devices. The materials involved in the fabrication process are usually sensitive to high temperature. Therefore, electroplating is often utilized as a post-CMOS process in deposition of the metallic materials, because the process temperature of electroplating is usually low. In addition, electroplating provides the easy and precise control of the properties of the deposited materials. Thus, we have developed MEMS devices fabricated by gold electroplating [2].

For application of the electroplated gold materials in MEMS devices, it is necessary to evaluate the structure stability and reliability of the materials in micro-scale, while there are very few reports on the above issues of the electroplated gold materials in micro-scale. In our previous study, the structure stability of micro-cantilevers made of electroplated gold upper layer and sputtered titanium bottom layer was evaluated by observing the deformation behavior when aspect ratio of the micro-cantilever was varied [3]. We reported that the Ti/Au two-layer structure was effective in improving the structure stability. In this paper, in order to clarify the mechanical characteristics, we compared with the results of the measurements and those of the FEM (Finite Element Method) analysis. The FEM analysis was carried out by using COMSOL.

The Ti/Au two-layer micro-cantilevers were modeled with different dimensions in the FEM analysis. The parameters of the structure and the material properties of the micro-cantilevers were as follows: length (L) was ranged from 100 to 1000 μm, width (W) was ranged from 5 to 15 μm, thickness of the gold layer was either 3, 10 or 12 μm with the constant value of the 0.1 μm titanium layer thickness, respectively, Young's modulus of titanium and gold were 115.7 and 70 GPa, respectively, thermal expansion coefficient of titanium and gold are 8.6×10^{-6} and 14.2×10^{-6} K^{-1}, respectively. The value of temperature was 310 °C which is the maximum temperature during MEMS fabrication. Based on these above condition, the FEM analysis was performed.

For all of the micro-cantilevers, the results of the FEM analysis showed the structure stability and downward tip deflections. The deflection was increased as the length of the micro-cantilevers increased. On the other hand, the deflection was reduced as the thickness of gold increased. These results of the FEM analysis were consistent with those of the observation of the Ti/Au two-layer micro-cantilevers [3]. From the view point of the magnitude of the deflection, the results of the FEM analysis were lager than those of the experiments, while the same deflection trends were observed. We could presume that the difference was caused by the intermetallic layer formed at the Ti/Au interface due to the temperature during the MEMS fabrication process. We would consider the intermetallic layer in the FEM analysis. In conclusion, it was revealed that the Ti/Au two-layer micro-cantilevers had the structure stability and the deformation was mostly contributed by the difference in thermal expansion of titanium and gold.

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Nitrophenyl Films on Few Layer Graphene (FLG): A Combined Electrochemistry, Spectroscopy and Microscopy Study

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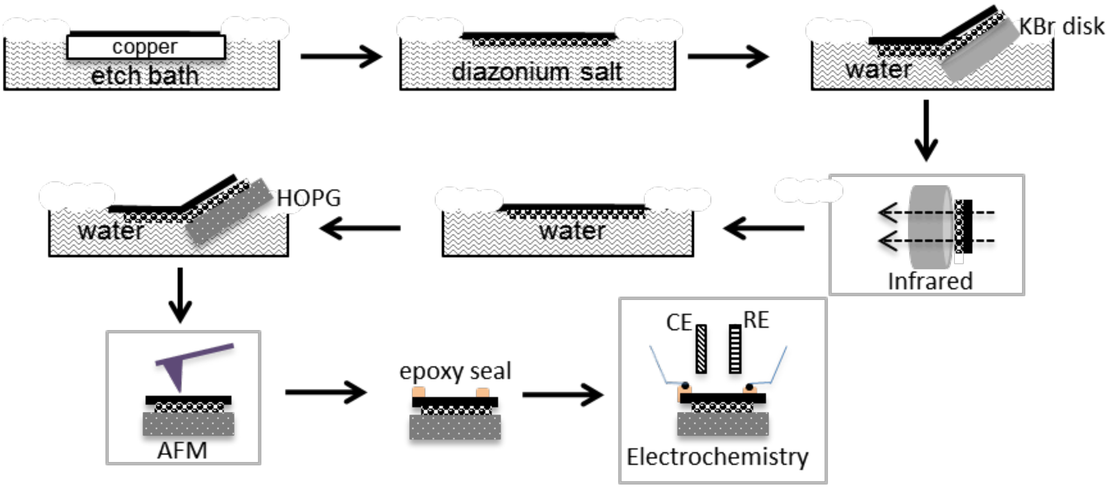
Single-layer and few layer graphene (FLG) sheets are difficult to handle and manipulate because of their high hydrophobicity and tendency to aggregate in solution. Chemical modification of the sheets can ameliorate these problems and also add useful functionality to the materials. Reaction with aryldiazonium salts at open-circuit potential is a simple and useful method for adding covalently bonded films to graphene however aspects of the deposited films have not been studied in detail.

In our work, we have developed a strategy that allows FLG, grown by chemical vapour deposition on copper foil, to be modified while on the Cu growth substrate and also free-floating in solution (Scheme 1). An advantage of our protocols is that infrared spectroscopy, atomic force microscopy and electrochemistry can all be performed on the *same* sample, revealing new information about the films. A further advantage of our methods is that for electrochemical studies, the nitrophenyl film can be sandwiched between the FLG substrate and HOPG. The film is accessible to electrolyte solution and we measure much higher concentrations of nitrophenyl groups than if the film is contacted from one side only (i.e. only through the FLG substrate).



Scheme 1. Protocol for the modification and subsequent analysis of free-floating, few-layer graphene

CNTs/Graphene Aerogel as Cathode Materials for Non-aqueous Lithium-Oxygen Batteries

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Abstract

$Li-O_2$ batteries have far higher theoretical energy density than lithium-ion batteries, which is an attractive energy storage device for electric vehicle applications [1-3]. Unlike lithium-ion batteries, a reaction of ideally reversible O_2 reduction and combination with Li+ occurs on the cathode of $Li-O_2$ batteries, thus a porous cathode is essential not only to provide pathways of electron, lithium ion, and O_2, but also to provide room for growth of Li_2O_2. Although carbon materials have been widely used as cathode materials in nonaqueous $Li-O_2$ batteries due to their high electrical conductivity and large surface areas [4-8], there is still no systematic research for the optimized design of carbon materials for ORR. Here, we report a CNTs/graphene aerogel as cathode materials via self-assembling process, in which graphene oxide sheets were used as "surfactant" to uniformly disperse CNTs, and CNTs was used as "spacers" to stabilize the graphene sheets from aggregation. This optimized carbon material can enhance the performance as cathode materials for $Li-O_2$batteries, which delivers much higher discharge capacity (4656mAh g^{-1}) compared with CNTs (3192mAh g^{-1}) and graphene aerogel (3579mAh g^{-1}) under identical conditions.

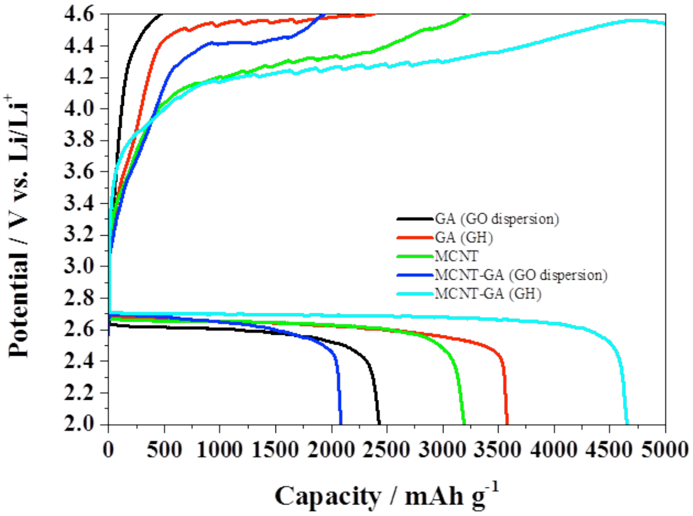

Figure 1. The first discharge/charge curves of $Li-O_2$ batteries using different graphene-based aerogels as cathodic materials, respectively, at a current density of 100 mA g^{-1} (equal to 0.1 mA cm^{-2}).

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Laser-ablated micropore glass membranes to modulate soft electrochemical interfaces

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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 µITIES arrays. This was achieved by laser ablation of 10 x 10 square arrays in ~130 µm thick borosilicate glass coverslips (Fig. 1A). The laser entry side presented pore diameters of *ca*. 50 µm and the exit side *ca*. 25 µm. 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 ~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.

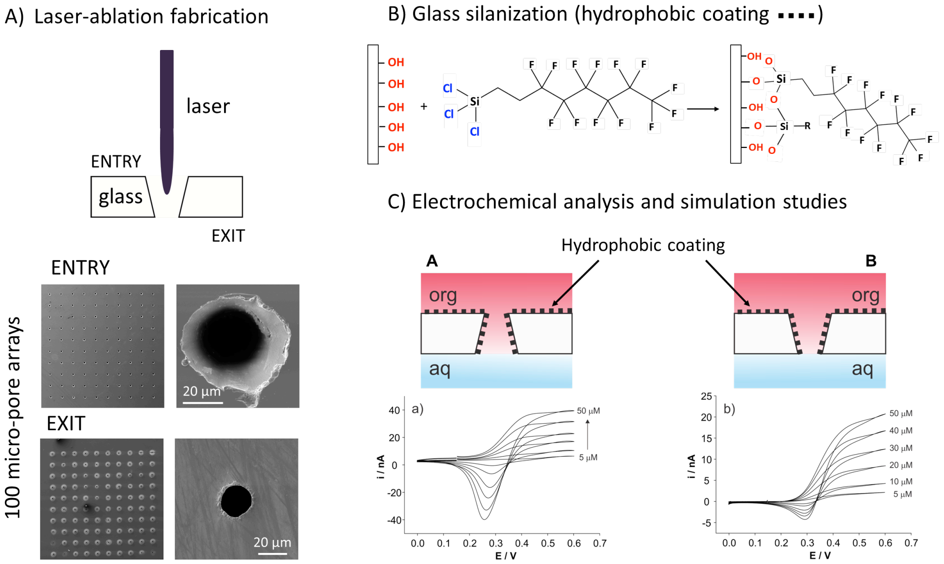

Figure 1. A) Sketch of the membrane fabrication and SEM images of the µ-pore array, B) silanization reaction to coat the glass membrane and C) voltammograms obtained for $TPrA^+$ transfer across water/1,6-dichlorohexane µ-interfaces formed with the different configurations of the glass µ-array.

Refining the Structure of Graphite Oxide: Selective Labelling and Voltammetric Quantification of Inherent Functional Groups

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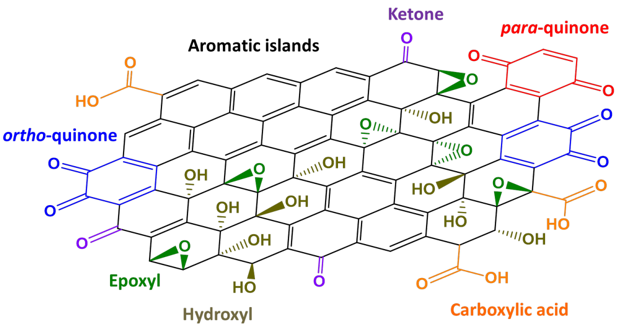
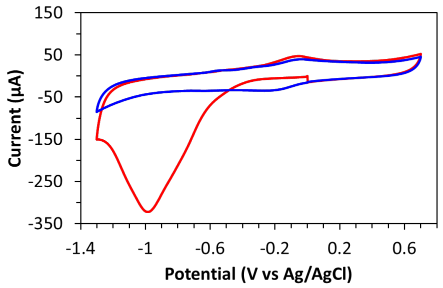
Chemical modification and functionalization of inherent functional groups within graphite oxide (GO) are interesting research aspects of graphene-type nano-materials used in wide-ranging applications. Despite extensive research, there remains some discrepancy in its structure, with current knowledge limited primarily to spectroscopic data from XPS, NMR and vibrational spectroscopies. We report herein an innovative electrochemistry-based approach. Four electroactive labels are chosen to selectively functionalize groups in GO, and quantification of each group is achieved by voltammetric analysis. This allows for the first time quantification of absolute amounts of each group, with a further advantage of distinguishing various carbonyl species: namely ortho- and para-quinones from aliphatic ketones. Intrinsic variations in the compositions of permanganate versus chlorate-oxidized GOs were thus observed, confirming previously observed differences in electrochemical character of the GOs. Principal differences include permanganate-GO exhibiting substantial quinonyl content, in comparison to chlorate-GO with the vast majority of its carbonyls as isolated ketones. The results confirm that carboxylic groups are rare in actuality, and are in fact entirely absent from chlorate-GO. These observations refine and advance our understanding of GO structures by addressing certain disparities in past models resulting from employment of different oxidation routes, with the vital implication that GO production methods cannot be used interchangeably in the manufacture of graphene-based devices.





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Antagonist Effects Leading to Enhanced Electrogenerated Chemiluminescence in Thermoresponsive Hydrogel Nanomaterials

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Particularly fascinating nanomaterials are stimuli-responsive hydrogels prepared as particles (called microgels) or films. The properties of such so-called "smart" materials are modulated by an external stimulus (e.g. temperature, pH, ionic strength, biomolecular recognition, light, etc.), which triggers expansion or contraction of the polymer network, at the origin of sensing capabilities [1]. So far, many luminescent hydrogels have been reported that are capable of transducing these swelling changes into a change in fluorescence intensity. Thanks to their unique stability, biocompatibity and softness, such systems have already been used successfully in sensing, such as intracellular temperature or pH measurement. However, examples of electrochemically-active microgels are scarce, although responsive polymers have gained an increasing interest over the last years. The combination of electrogenerated chemiluminescence (ECL) with stimuli-responsive hydrogels offers the opportunity to design novel nanoparticles and thin films whose electrochemistry and ECL are manipulated not only by the electrode potential but also by an external stimulus.

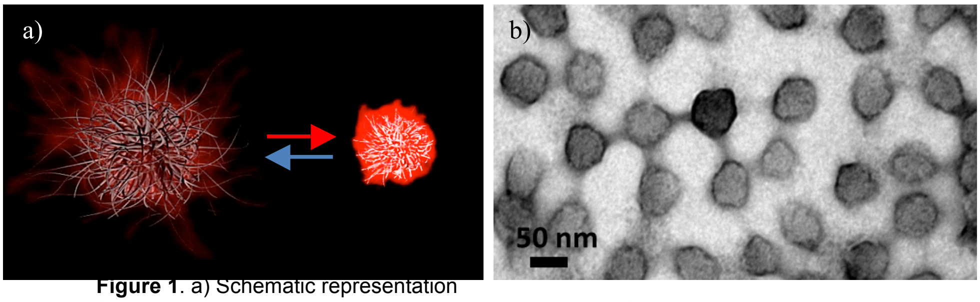

Figure 1. a) Schematic representation of the thermoresponsive ECL microgels in the swollen (left) and collapsed (right) states. b) Transmission electron microscopy image of dried microgels.

In the first part of this work, through a rational choice of model ECL and stimuli-sensitive microgel systems (Fig. 1), electrochemistry and ECL of thermoresponsive 100-nm microgels are reported. We demonstrated an unexpected enhancement of the ECL signal which occurs at the swell-collapse transition of the microgel particles. ECL signals are enhanced up to 2 orders of magnitude and this reversible phenomenon correlates with the swell-collapse transition of the microgels [2]. It is noteworthy that this turn-on signal with increasing temperature is extremely rare with other thermoresponsive luminescent systems. This unexpected behavior is related to the microgel shrinking, which decreases the average distance between adjacent redox sites. In addition, tunable multicolor systems have been developed based on resonance energy transfer mechanisms using ECL luminophore as the donor system [3]. In the second part, electrodes were modified with a thermoresponsive redox hydrogel film incorporating $Ru(bpy)_3^{2+}$ by electrochemically assisted free radical polymerization. The resulting thin films lead also to enhancement of the ECL signal even if antagonist effects due to the blocked diffusion of the co-reactant species were observed [4]. The versatility of ECL coupled to stimuli-responsive materials allows developing the use of the same principle with other types of stimuli and also the design of new multifunctional nanoparticles and modified interfaces.

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Electrochemical Investigations of Deposited Quantum Rods. Intrinsic Properties and Substrate Effects.

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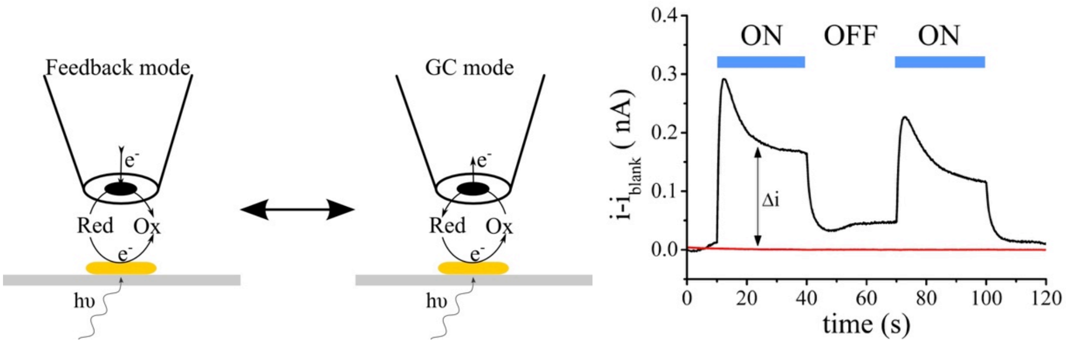
Since the first report concerning solar water splitting, research concerning a suitable material for this reaction is a very active domain.[1] Core-shell semiconductor nanoparticles as those prepared from CdSe-CdS appear as promising materials to obtain an efficient charge separation under illumination. Classical method for studying the reactivity of the photo-excited electrons involves the immobilization of the nano-object over a metallic surface (generally a gold surface) that plays the role of a sensitized photo-electrode that is investigated by classical electrochemical methods.[2,3] In this context, Scanning Electrochemical Microscopy (SECM) has been shown as a powerful method to study photo-electrochemical systems with the advantage that the photoelectroactive surface is seen from the solution size through the reaction with a molecular probe. It results less constrain concerning the nature of substrate on which the QRs are deposited.

In this work, the electrochemical properties of deposited films of CdSe-CdS quantum rods (QRs) have been examined using SECM in feedback and generation-collection modes using series of molecular probes. Notably, the method enables the interrogation of quantum rods deposition without the interference of photo-ejection of electrons inherent to the electrode material and more important without the coupling between both processes.[4] Influences of different redox scavengers like O_2 or the solvent itself were also examined to draw a complete view of the reactive properties of the QRs.

As expected, the results show that the apparent redox properties of QRs as regeneration rates or reduction strength upon illumination strongly depend on the nature of the substrate. However, no oxidation reaction has been demonstrated, asking the question of the occurrence of parallel reactions, possibly occurring inside the rods. This put in light the strongly reductive properties of quantum rods under irradiation without the influence of other materials and provides an interesting possibility for tuning the properties of the QRs themselves but also for preparing sensitized-surfaces on which QRs are immobilized.



SECM chronoamperometry on a gold microelectrode at a fixed distance of a QRs film deposited on a transparent substrate and using ferrocene as mediator.

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Electrochemistry and Applications of Modified Electrodes Based on Metal Nanoclusters

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Thiolate-protected metal nanoclusters have attracted significant research interest recently because of promises offered by their unique catalytic, optical, and electrochemical properties. These clusters have special stability at certain compositions and thus atomically precise clusters are typically obtained from a variety of size-selective syntheses. This presentation reports electrochemical and optical properties of these nanoclusters and their use in electrochemical sensing and catalysis. Voltammetry of these nanoclusters exhibited well-resolved, reversible redox peaks and size-dependent electrochemical HOMO-LUMO gaps that could be correlated to optical and calculated energy gaps. These nanoclusters also showed excellent electrocatalytic activity toward oxidation of biologically relevant analytes. The modified electrode film prepared with Au_{25} nanoclusters exhibited excellent mediated electrocatalytic activity that was utilized for amperometric sensing of dopamine and glucose. The electron transfer dynamics in the Au_{25} film was examined as a function of Au_{25} concentration, which manifested the dual role of Au_{25} as an electronic conductor as well as a redox mediator. The electron transfer study has further revealed the correlation between the electronic conductivity of the Au_{25} film and the sensing sensitivity.

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The influence of composition Pd alloys on hydrogen electrosorption

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Palladium and its alloys with Rh, Ru and Pt represent a large group of materials absorbing hydrogen. Similar systems with less expensive metals can be used in batteries, fuel cells or for hydrogen storage. Since hydrogen can be electrochemically introduced and remove into/from Pd-based electrodes, such materials can be treated as charging-discharging systems in electrochemical capacitors [1] The method LVE has been applied in the study of hydrogen electrosorption in thin layers of Pd alloys [2]. Binary and ternary Pd alloys were prepared by electrodeposition on Au from baths containing Pd, Rh, Pt and Ru salts. The thickness of the deposited layers was in the range of 0.2 - 1 μm. The alloy formation was proved with the use of energy dispersive X-ray spectroscopy and X-ray diffraction. The Pd-rich binary alloys with Rh or Ru showed higher H absorption capacities in comparison to Pd. This fact can be explained by a favorable electrons effect due to alloy formation. The values of specific pseudocapacitance, power and energy were calculated for Pd-rich electrodes saturated with hydrogen in the dependence of temperature range. The maximum values of specific pseudocapacitance are for alloys with Rh and Ru with high specific energy. The highest specific power was obtained for Pd - alloys containing Pt additives. The formation of Pd–Ru–Rh alloys was confirmed electrochemically through the examination of sample properties in the acidic solution with the use of cyclic voltammetry. The XRD results show that the lattice parameter of the Pd–Ru–Rh alloy is smaller than that of Pd, i.e. Pd, Ru and Rh form contracted alloys. This is also mirrored in the course of hydrogen absorption curves (H/M vs. E), with the α–β phase transition region shifted into lower potentials. Pd–Ru–Rh alloys with ca. 98.5% Pd in the bulk absorb ca. 11% more hydrogen than pure Pd. In the process of electrochemical aging, the surface and bulk of Pd–Ru–Rh electrodes becomes enriched with Pd due to the preferential electrochemical dissolution of Ru and Rh. Thermodynamic parameters of hydride formation and decomposition in alloys were calculated from the potentials of the α→β and β→α phase transitions. The values of specific pseudocapacitance, specific energy and specific power of ternary alloys with Pd, Rh and Ru have been calculated. The electrochemical behavior of hybrid system containing AB_5 alloy and LVE electrode based on Pd alloys is also presented.

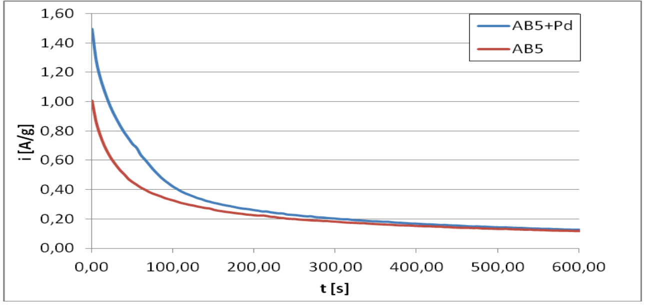

Fig. 1. Current vs. time dependence obtained in 6M KOH during discharging of the anode hybrid system $H/(Pd+ AB_5)$ and H/AB_5

Acknowledgment
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Electrochemical properties of surface modified manganese-based powders for lithium-ion battery

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Recently, large growth of mobile devices users and production of hybrid electric vehicles (HEV) and electric vehicles (EV) pushed researchers to develop new power storage devices with high energy density and high power. Lithium-ion batteries were found to be the most promising systems to conquer that challenges, due to high power capacity, good cyclability, flat charge/discharge profiles and high operating voltage. However, high costs of the electrode materials, low current densities acquired from the cells and safety concerns make Li-ion systems as still demanding improvement.

Among various electrode materials examined as a cathode in lithium-ion battery, manganese-based compounds are favourable due to high natural abundant, low cost and environmental friendliness of manganese chemical element. There have been performed a numerous studies on electrochemical properties of manganese oxides, olivines and silicates since last twenty years, although only few of them is used in large scale commercial battery. The reason of theirs inapplicability results from either low intrinsic conductivity (silicates and olivines) or structural instability (oxides). There are various strategies for eliminating these disadvantages, like coating grains with conductive layers, ion-doping, dispersion of metallic particles on the surface of material or oxide coatings preventing dissolution of active material in electrolyte.

In this work we present the syntheses and electrochemical properties of lithium-manganese oxide of spinel structure ($LiMn_2O_4$ LMO) and lithium manganese orthosilicate (Li_2MnSiO_4 LMS). The electrochemical properties of samples were examined in three-electrode Swagelok-type cell with synthesised material as working electrode and lithium as a counter and reference electrode. The research contains the comparison of electrochemical parameters of Li_2MnSiO_4 and $LiMn_2O_4$. The determination of lithium diffusion coefficient, specific capacity, lithium intercalation potential, coulombic efficiency and capacity retention allow to evaluate the potential applicability of LMS in lithium-ion battery.

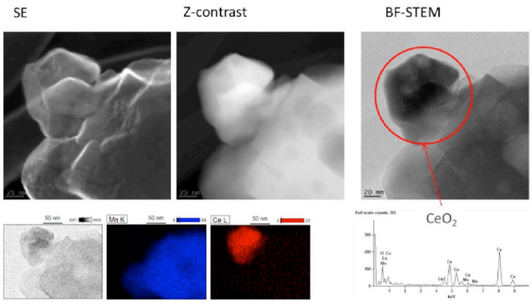

Fig 1. Structure of LMO/CeO_2 powder imaged in SE, Z-contrast and BF-STEM modes (top). Distribution of chemical elements on the surface of particles (bottom).

In addition LMO grains have been surface modified by CeO_2 (Fig. 1) or metallic silver nanoparticles. Surface modification of $LiMn_2O_4$ grains' by using 1%wt. of cerium dioxide admixture improved cycling stability and capacity retention and revealed only 2% capacity loss after 100 cycles when discharged at 1 C. On the other hand, Ag nanoparticles uniformly dispersed in the LMO surface tend to electrodissolve at electrode potential higher than 3,5 V (vs Li/Li^+) which resulted in series of side reactions in the cell.

Acknowledgments:
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The calcareous deposit formed under cathodic polarization as a contaminant monitoring device in seawater

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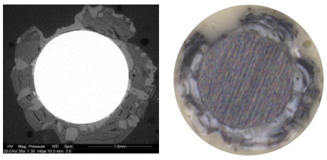
The contamination of coastal waters by trace metals is an important worldwide concern. Although metals are natural part of the environment, their release to coastal waters may significantly affect the productivity and diversity of lagoon ecosystems. This is particularly true in New Caledonia, where soils are highly enriched in nickel and other metals and subjected to intense mining extraction and strong erosion due to tropical rainfall. In this context, a novel use of the calcareous deposit formed under the cathodic protection of a metallic structure is proposed to monitor the seawater contamination by metals.

In our experiments, the calcareous deposit is formed by cathodic current density to force electrochemistry reactions (reduction of dissolved oxygen and water). Whatever the current density, the working electrode's potential reaches potential in the water reduction range giving rise to H_2 bubbling. This phenomenon will inhibit the electrode blocking by the formation of a calcareous deposit at its surface. A voluminous deposit, composed of $CaCO_3$ and $Mg(OH)_2$, could then grow with time.

The goals of these experiments are to understand the extent of integration inside the deposit of metallic contaminants present under their ionic form in seawater. Following the trapped amount, the agglomerate could monitor the seawater pollution. The incorporation of nickel that could be rejected is firstly studied, considering the New Caledonia context. Experiments are then performed in artificial seawater and containing different amount of ionic nickel (from 0,4 to 27,7 mg/L). A large volume (2 L) is used, avoiding variations of species concentrations during the formation of deposits. The working electrode was commercial galvanised steel wire and a current density of -300 µA/cm² was applied.

The calcareous deposit has been analysed by scanning electron microscopy (SEM) and µ-Raman spectroscopy (surface and cross section) and by X-Ray diffraction. Our results show the presence of nickel incorporated as $Ni(OH)_2$ in the calcareous deposit and the formation of a pure $CaCO_3$ (aragonite) layer at the surface. The calcareous deposit formed under cathodic polarization is thus a promising tool for contaminant monitoring in seawater.

This work is funded by the French Research National Agency (ANR) and is a part of the project "EcoCorail".



Electrocatalytic Behaviour of Nanocomposites of Electropolymerized Cobalt Phthalocyanines Supported on Multi-walled Carbon Nanotubes Modified Glassy Carbon Electrode.

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Abstract

Thin films of MPcs on solid electrode surfaces have been fabricated by different pathways including adsorption **[1],** electropolymerization **[2,3]** and click chemistry **[4]** to name just a few. In this work, an electrocatalytic platform was fabricated in two steps: (i) drop-drying multiwalled carbon nanotubes (MWCNTs) on a glassy carbon electrode (GCE) and (ii) electropolymerisation of tetra(4-(4,6-diaminopyrimidin-2-ylthio) cobalt(II) phthalocyanine (CoPyPc). Polymerization is more reliable, often reproducible than adsorption and the thickness of the film can be controlled by the number of polymer cycles. CoPyPc has polymerizable groups on the substituent and we use X-ray photoelectron spectroscopy (XPS) to confirm the point of polymerization. We compare the electrocatalytic activities of the adsorbed and polymerized complexes. Cyclic voltammetry (CV), chronoamperometry (CA), and rotating disk electrode (RDE) studies were used for electrochemical characterization of the prepared polymer of CoPyPc and its nanocomposites. The electrocatalytic activity of the polymerized CoPyPc was found to be superior when polymerization was done on top of MWCNT than bare glassy carbon electrode. This was tested using thiol oxidation. The scheme for preparation of polymerized CoPyPc-MWCNT nanocomposite is shown in Fig.1.

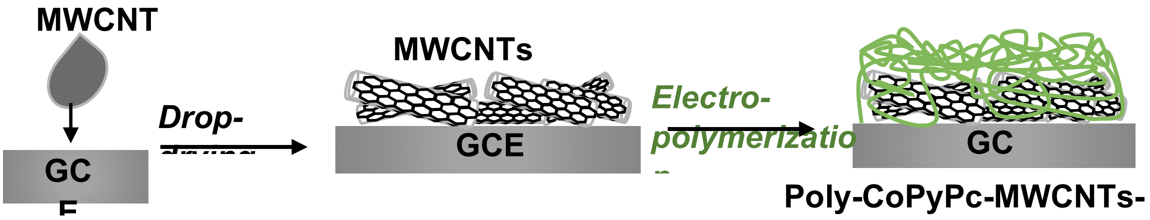

Fig.1: Preparation of Poly-CoPyPc-MWCNTs nanocomposite on GCE**.**

: Electrocatalysis, thiol oxidation, electropolymerisation, poly-cobalt phthalocyanine derivative, MWCNT.

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Electrochemical Potential of Bioreduced Silver Nanoparticles

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Hazards and toxicity associated with the physical and chemical synthesis protocol of metal nanoparticles has recently led researchers to seek alternative routes that is eco-friendly, cheap and fast; the green chemistry approach where plant extracts and microorganism are used in the bioreduction of the metal salt or oxide is fast gaining popularity in the field of nanobiotechnology[1, 2]. However, controversy still trails its acceptability due to stoichiometry; furthermore, electrochemical studies on these metal nanoparticles are limited [3, 4]. In this study silver nitrate was reduced to its "nanoform" through a one-step synthesis protocol using the leaf extract of *senna obtusifolia*. The usual microscopic and spectroscopic techniques such as UV-vis., FTIR and AFM were used to confirm the formation of silver nanoparticles. Electrochemical characterization using cyclic voltammetry and impedance spectroscopy further reveals the formation of silver nanoparticles via the redox reaction: $Ag^{+} + e^{-} \rightarrow Ag$ (Fig.1) with a formal potential value of 0.61 V vs. Ag|AgCl 3 M KCl. Preliminary study on possible application of the nanoparticles for glucose oxidation was also carried out (Fig. 2). For the first time, we are able to establish the formation of biosynthesized silver nanoparticles using electrochemical techniques with potential application for the fabrication of biosensor.

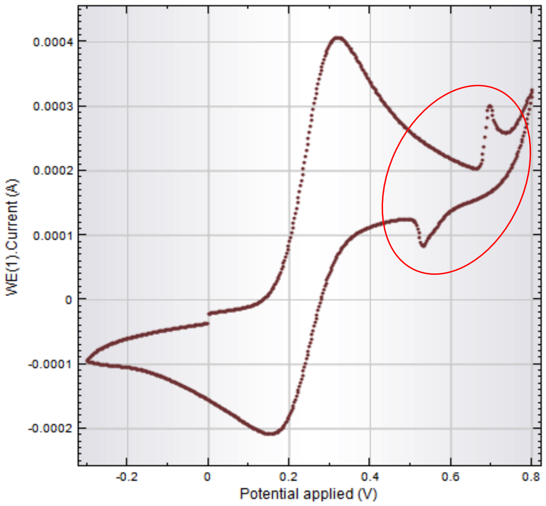

Fig. 1

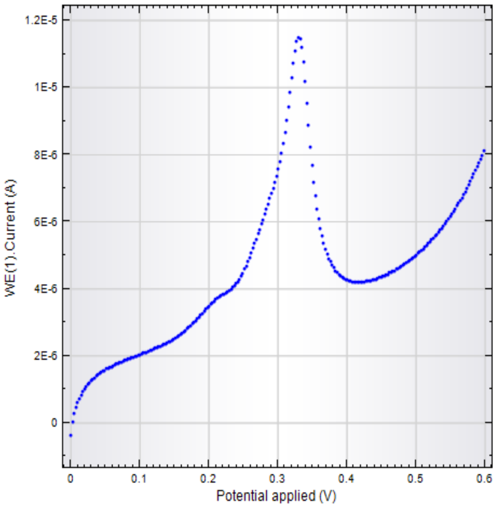

Fig. 2

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A Study of the Interface between a New CoCrNbMoZr Alloy and Artificial Saliva

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The microstructure, mechanical and anticorrosive properties of the new CoCrNbMoZr alloy were studied in comparison with a commercial CoCrMo alloy. Structural and microstructural characterisation were performed by the scanning electron microscopy, SEM and X-ray diffraction, XRD analyses. Mechanical properties were determined by traction test from the stress-strain curve. The main electrochemical parameters were evaluated from the cyclic potentiodynamic polarisation curves; the main corrosion parameters were estimated from the linear polarisation measurements; electrochemical impedance spectra (Nyquist and Bode) were displayed at open circuit potential; monitoring of the open circuit potentials ranged for a period of 1000 immersion hours in Carter-Brugirard artificial saliva.

The cast CoCrNbMoZr alloy shows a multicomponent, fine dendritic structure with typical interdendritic distances between few and 20 micron (SEM); EDS spectra detected the alloying elements, Co, Cr, Nb, Mo, Mn, Si, Zr; EDS analysis of the interdendritic regions revealed that they are enriched in Mo, Nb, Si and C. The XRD pattern was indexed to a biphase structure composed of two cobalt-based phases, one with hexagonally packed structure (*h*), and the secondary with second hexagonal structure (*h'*) that corresponds to that reported for cobalt-chromium-niobium alloy. The Young's modulus of the new alloy has a value very close with that of the maxilla bone.

Corrosion, passivation and transpassive potentials have more electropositive values for the new alloy as compared with the commercial one; this fact is due to the more resistant passive film existing on the new alloy surface that is formed from the chromium and molybdenum oxides (existing on CoCrMo alloy surface, as well), and, in addition, the very protective niobium and zirconium oxides which were detected by XPS analysis. Transpassive potentials are situated at nobler values of about +750 mV (vs. SCE) for the new CoCrNbMoZr alloy; some authors sustained that the body potential vary around +400 ÷ +500 mV (vs. SCE); in this case, E_T values for the both studied metals exceed these values, assuring a good protection against the aggressive ions from saliva. Tendency to passivation have lower values for the new CoCrNbMoZr alloy showing a better, more rapid, easier passivation as result of the more compact, denser passive film. Medium values of the passive current densities are lower for the new alloy due to the same protective passive film.

Corrosion current densities and corrosion rates are about two times lower for the new alloy as compared with the commercial alloy, demonstrating a higher resistance to corrosion; polarisation resistances of the new alloy are 2-3 times higher than those of the comparing alloy, that signify a more stable, passive layer, as result of the beneficial effect of Nb and Zr elements by increase of the corrosion resistance.

Nyquist plots are represented by the open arches which attest capacitors, passive films with insulating properties for the both studied materials; the diameters of the arches are higher for the new CoCrNbMoZr alloy, indicating that its passive film is a better insulator with the higher protective properties than those of CoCrMo alloy. Bode phase angle plots for the commercial and new alloy display one peak, one phase angle on a large frequency range in all Carter-Brugirard saliva; the phase angles have bigger values for the new CoCrNbMoZr alloy, indicative of more protective, more compact passive film existing on this alloy surface. The experimental results were modelled with an electric equivalent circuit with two time constants describing the passive film.

Taking into consideration the microstructural features, electrochemical behaviour, corrosion resistance, mechanical characteristics, it results that the new CoCrNbMoZr alloy is recommended as a promising, innovative alloy for the dental applications.

Highly Porous Electro-Deposited Pt-Ru, Pt-Pd, and Pt-Au Electrodes for the Electro-Oxidation of Methanol, Formic Acid, and Glucose

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We present an electro-deposition process for the fabrication of highly porous Pt-Ru, Pt-Pd and Pt-Au electrodes. The process is based on our previous works where Pt and Cu have been co-deposited from an aqueous electrolyte. Upon subsequent selective Cu dissolution at an oxidative potential a highly porous Pt electrode can be obtained [1, 2]. In the present work, a second noble metal was added to the electrolyte. The specific surface area and the electrochemical properties of various combinations of platinum and a second noble metal are compared for their applicability in methanol, formic acid and glucose fuel cells. We can show that the combination of two metals can enhance the electro-oxidation properties of the electrode.

In contrast to the previous work [2], an electrolyte containing also a second noble metal (Ru, Pd, or Au) in addition to platinum and copper was used for electrode fabrication. The molar ratios of the metals in the Pt-Pd and Pt-Au electrolytes were 4:1, 1:1, and 1:4; for Pt-Ru electrolytes ratios of 1:1, 1:10, and 1:20 were used. To yield mechanically stable deposits, only 600 instead of 1200 deposition pulses were applied.

Despite the same number of deposition pulses, the electrode roughness factors (RF, ratio between specific and geometrical area) vary from about 500 (Pt-Ru(1:20)) to 4700 (Pt-Pd(4:1)). For comparison, the previous state-of-the-art platinum electrodes (1200 pulses) yielded RFs of 6500 ± 700 [2]. The concentration of the second noble metal in the electrolyte has a distinct influence on microstructure, as shown exemplarily for Pt-Au in Fig. 1. Energy-dispersive X-ray spectroscopy reveals that the ratio of the metals in the electrolyte does not correspond to the ratio of the metals deposited on the electrode.

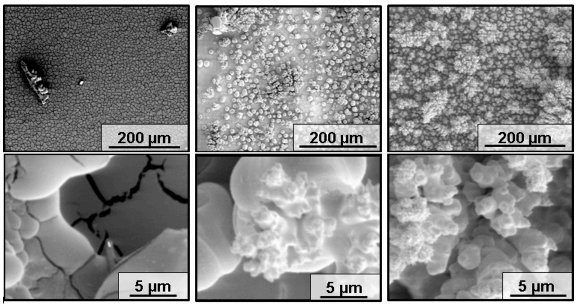

Fig.1: SEM pictures for Pt-Au electrodes as an example. Electrodes are made from electrolytes containing Pt and Au in a ratio of 4:1 (left column), 1:1 (middle column) and 1:4 (right column).

Regarding the electro-oxidation of methanol, Pt-Ru(1:1) electrodes exhibit current densities of 11 ± 2 mA/cm^2 at a potential of 355 mV vs SCE after 30 min. The other Pt-Ru electrodes show lower current densities in the same range as the various Pt-Pd and Pt-Au electrodes. In formic acid, all of the Pt-Pd electrodes and Pt-Ru(1:1) reach more than 30 mA/cm^2 at 400 mV vs SCE after 30 min. The other Pt-Ru and all of the Pt-Au electrodes exhibit only between 8 and 24 mA/cm^2. Since glucose oxidation anodes are subject to significant poisoning, their long-term performance at -200 mV vs SCE has been evaluated after 8 days of continuous operation in phosphate buffered saline containing 3 mM glucose. Here, the Pt-Au(1:4) electrodes with a RF of 2904 ± 627 show 16 ± 14 µA/cm^2. This value corresponds to the previous state-of-the-art electrode with a much higher RF of 6500 ±700 [2]. It is therefore expected, that Pt-Au(1:4) electrodes with increased RF will show better performance. However, these electrodes also exhibit a large variation, presumably due to a not yet well controlled parameter in the fabrication process. Future work will thus be focused to optimize the fabrication process and also to yield mechanically stable electrodes with increased specific surface area.

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Chemical Treatment of a new Ti-Zr-Nb Alloy Surface by Applying Hydroxyapatite Coating

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The hydroxyapatite (HA) coating was deposited on the new Ti-15Zr-5Nb alloy surface by a chemical method; its composition was determined by Raman micro-spectroscopy and X-ray photoelectron spectroscopy (XPS), and its microstructure, topography and roughness by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The electrochemical behaviour and corrosion resistance of this coating in simulated physiological biofluids were studied by cyclic potentiodynamic and linear polarization methods and electrochemical impedance spectroscopy (EIS).

Raman spectra clearly detected the main characteristic features for crystalline HA; the XPS spectra identified the existence of the core levels for Ca 2p, P 2p, O 1s specific for HA. The thickness of the deposited layer is 16.5 ± 1.0 nm; this thickness is double than that of the native passive film of 8.0 ± 1.0 nm. The SEM micrographs revealed a coating formed by spherical particles with diameter of about 100 nm and height of about 200 nm. The 2D and 3D AFM images indicated a rough surface that can facilitate the adhesion and proliferation of the osteoblast cells.

From Raman micro-spectroscopy, XPS, SEM and AFM studies clearly resulted that the HA coating has an optimal crystalline microstructure with high roughness, which confer it the ability to form direct bonds with bone cells and to shorten the ossteointegration tim; also, this coating has a very good adherence of about 20 MPa.

All main electrochemical parameters have more favourable values for the HA coated alloy, more electropositive values of the corrosion and passivation potentials and lower values of the tendency to passivation and passive current density; these facts are due to the protective effect of the HA coating that thickened the native passive film and together acted as a barrier against the ion diffusion. The corrosion parameters showed that for the HA coated alloy, the corrosion current density and rate have values of about 7 times lower than those of bare alloy, denoting the better protective properties of the HA coating which reduced very much the ion release, conferring a very low toxicity.

The impedance Nyquist plots presented large semicircles, with the higher curvature radii for HA coated alloy than those of bare alloy, namely, a more insulating layer. The Bode phase angle plots for the HA coated alloy displayed two phase angles in the low frequency range and a phase angle in the high frequency range; bare alloy exhibited only two phase angles in the low frequency domain. The spectra for the bare alloy were modelled with an electric equivalent circuit with two time constants: the first time constant for the inner, barrier, insulating layer; the second time constant for the outer, less resistant, porous layer. For the HA coated alloy, an electric equivalent circuit with three time constants was fitted: the compact oxide layer, the porous oxide layer and the hydroxyapatite porous layer. Impedance results evinced the dual character of the coating: resistance to corrosion due to its inner oxide layer and bioactivity due to its outer porous HA layer.

The open circuit potentials both for the bare and coated alloy moved to more electropositive values over time, due to growth, thickening of the films on their surfaces; the fact that the E_{oc} values did not decreased in time shows that on the studied material surfaces did not take place activation, dissolution processes. For the HA coated alloy, more electropositive E_{oc} values than those on bare alloy were registered, demonstrating a more stable, resistant layer, namely, the HA coating has superior protective characteristics and assures long-term stability.

All results confirmed that the hydroxyapatite coating has strong passivation ability, protects the surrounding tissues from ion release or harmful compounds, avoiding the adverse reactions, stimulates the alloy stabilization within the bone and shortens the ossteointegration time.

Modification of the New Ti-Ta-Zr alloy surface by electrodeposition. Electrochemical and structural characterization of obtained nanolayer

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The anodic galvanostatic electrodeposition on new Ti15Ta-5Zr alloy surface was applied in H_3PO_4 solutions of different concentrations, 0.5M – 1.5M, at anodic current densities varying between 5 mA/cm^2 and 15 mA/cm^2, for various time periods from 15 min. till 90 min.

The composition and thickness of the electrodeposited nanolayer was analyzed by X-ray Photoelectron Spectroscopy (XPS), its topography and roughness by Atomic Force Microscopy (AFM), and its microstructure, morphology and porosity by Scanning Electron Microscopy (SEM). Electrochemical and corrosion behaviour of the most favourable electrodeposited nanolayer was examined by cyclic potentiodynamic and linear polarization methods and electrochemical impedance spectroscopy (EIS) in Ringer solution of different pH values, simulating the human biofluid.

XPS analysis showed that the nanolayer obtained by the electrodeposition in 1.1M H_3PO_4 solution at a current density of 12 mA/cm^2 for a period of 50 min. had the most convenient composition and thickness. XPS spectra identified the binding energies for Ti 2p, Ta 4f, Zr 3d (the constituent elements of Ti-15Ta-5Zr alloy), and, in addition, O 1s and P 2p incorporated from the electrolyte. The surface of Ti-15Ta-5Zr alloy was covered with a nanolayer formed by TiO_2, ZrO_2 oxides, tantalum suboxides and PO_4^{3-} ions. The thickness of the electrodeposited layer was 15.5 nm ± 1.0 nm; comparing with the thickness of 8.5 nm ± 1 nm of the alloy native passive film, it appears that, the new layer doubled its thickness. AFM 3D images revealed a rough nanolayer with homogeneous roughness and porosity. SEM micrographs presented a porous microstructure with fine porosity and pore diameter of 20 – 50 nm. From XPS, AFM and SEM analysis resulted that on the new Ti-15Ta-5Zr alloy surface was electrodeposited a phosphorous-enriched oxide nanolayer with very good roughness and porosity.

The corrosion and passivation potentials for the anodic oxidized alloy shifted towards positive region in comparison with those of the bare alloy, evincing a nobler surface; this fact can be explained by the thicker oxide layer and by its composition enriched with phosphorous ions which inhibit the dissolution processes at the interface. Also, the passive current density had lower values proving that the electrodeposited nanolayer acts as an effective barrier against the aggressive ion entrance through it. Tendency to passivation had lower values as result of the strong passivation action exercised by the electrodeposited nanolayer. All corrosion parameters presented pronounced decrease (about 7 times) for the values of corrosion current density and rates and the total quantity of ions released into physiological Ringer solutions, namely, the toxicity of the treated alloy is much lower than that of the bare one.

Nyquist spectra displayed larger semicircles with bigger radii and higher impedance values for the oxidized alloy in comparison with the bare one; these facts show a capacitive behaviour, a film with dielectric properties and that the electrodeposited nanolayer has more insulating, more protective properties than that on the bare alloy. Bode phase angle plots revealed in the low and middle frequency range two phase angles with very high values describing the same capacitive behaviour. The anodic oxidized alloy had higher phase angles, with 2^o – 3^o higher than those of the bare one indicating a protective film with better anticorrosive resistance conferred by the thicker electrodeposited nanolayer. EIS spectra were modelled with two time constant equivalent electric circuit which reflects the barrier properties of the inner, dense, compact layer and those of porosity of the outer, less protective porous layer where can take place dissolution and deposition processes, interactions with .the surrounding environment, i.e. bioactivity.

The electrodeposited nanolayer is able to protect the alloy from ion release, to assure long-term corrosion resistance, to minimize adverse reactions, to increase the alloy bioactivity, to stimulate the cell growth and to favour the osseointegration.

Functionalisation of new Ti-Zr-Ta-Ag alloy surface by deposition of antibacterial nanoparticles

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Silver nanoparticle sonochemical deposition was performed irradiating the new Ti-Zr-Ta-Ag alloy surface immersed in a water based solution of silver nitrate. The deposition of Ag nanoparticles on the alloy surface was analysed by SEM images and EDX chemical analysis (Fig. 1). SEM showed the silver nanoparticles as white spots on the grey background of the alloy. The size of the deposited nanoparticules can be modulated with the experimental parameters of the sonochemical deposition, namely the concentration of the silver nitrate solution, the type of solvent and irradiating time. A nanocoating with moderate density of Ag nanoparticles and size of about 50 nm was obtained.

SEM images of the Ti-Zr-Ta-Ag alloy surface after sonochemical deposition of Ag nanoparticles and EDX spectra showing the elemental composition.

The improvement of all corrosion parameters for the antibacterial processed alloy as compared with bare one, in simulated biofluid was observed, due to the effect of the nanocoating to reduce the effective active areas by the action of the efficient passive layer. The processed alloy presented a decrease of the corrosion current density, corrosion rate and ion release rate and an increase of the polarisation resistance over time; on the contrary, for the bare alloy, all these parameters slowly became more unfavourable in time as result of a low susceptibility to corrosion.

The monitoring of electrochemical behaviour of the coated alloy in comparison with that of the bare alloy was studied from cyclic potentiodynamic polarisation curves: corrosion and passivation potentials had nobler values that means a more compact, thicker, more protective passive film; the tendency to passivation had lower values, namely an easier, rapid passivation conferred by the Ag nanoparticles; passivation current density is about 2 times lower than that of bare alloy proving a more resistant passive film. Over time, all electrochemical parameters improved their values for the processed alloy and deteriorated their values for the bare one. The Ag nanoparticles sonochemicaly deposited on the new alloy surface enhanced its corrosion resistance and maintained over time this resistance.

SEM observations revealed that the nanocoating had a stable microstucture in time; EDX spectra detected a decrease of Ag line intensity comparing with that of the initial nanocoating, fact that signifies the dissolution of the silver nanoparticles i.e. they accomplished their action as antibacterial factor.

The viability and adhesion capacity of the L929 cells was good; also, their morphology evoluated well in time. The antibacterial activity of Ag nanoparticles against the Staphylococcus Aureus is about 60%, namely, a very good effect of inhibition of the bacterial attack.

Activity and Selectivity of Unsupported Pt, Rh and Pt-Rh Nanocatalysts towards Oxidation of Ethanol to CO_2, Acetic Acid and Acetaldehyde

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Electrooxidation of ethanol on noble metals is broadly studied due to its potential application in low temperature direct ethanol fuel cells (DEFCs). However there is no known ethanol electrooxidation reaction (EOR) catalyst, allowing for complete electrooxidation of ethanol to CO_2. Even for the most active systems, incomplete and slow EOR renders the DEFCs not economically viable. Therefore search for more selective and active catalysts in EOR is still open. It was shown that nanoalloys of platinum with other metals, such as Ru or Sn, enhance catalytic activity of Pt in EOR in terms of catalytic current density.

However, despite the higher current, addition of Ru or Sn to Pt further decrease the already small amount of CO_2, produced in EOR on pure Pt. Selectivity of a given catalyst towards CO_2 in EOR is especially important, due to the facts, that CO_2 is the product of complete, 12-electron oxidation of ethanol molecule, where acetaldehyde and acetic acid (other possible products) yields respectively 2- or 4-electrons. Additionally acetic acid cannot be further oxidized in a working fuel cell, thus it is effectively a dead-end of EOR in a working low temperature DEFC. As a result other catalysts, more active and selective toward ethanol electrooxidation to CO_2 are needed for a commercially viable DEFC.

In this context investigation of Pt-Rh nanoalloys are very interesting because of reported activation of C-C bond in ethanol and production of larger amount of CO_2 in EOR. However the DEMS studies on CO_2 production on Pt-Rh were limited to narrow range of systems. In particular all previous DEMS (differential electrochemical mass spectrometry) studies were done on carbon-supported Pt-Rh nanoparticles or co-deposited Pt-Rh layers and the Rh content was usually close to 50%.

Here we will report the results of investigation of the electrocatalytic activity of unsupported Pt-Rh nanocatalysts towards EOR. Nanoparticles used covered the whole (0-100 at. %) Rh concentration range. The use of unsupported, ultra-pure nanoparticles allowed for addressing the impact of possible changes in either surface morphology or electronic properties on mechanism of EOR. Special care was taken to precisely determine the electrochemically active surface area, which in turn allowed us to pinpoint the surface normalized catalytic activity. Using DEMS experiments we determined how the amounts of produced carbon dioxide, acetaldehyde and acetic acid (the most important products of ethanol electrocatalytic oxidation) per active surface area changed as a function of nanoparticle composition and how it impacted the onset potential for particular products. As a result we were able to comment on the selectivity of unsupported Pt-Rh nanoalloys in EOR as well as on the activity of this material in C-C bond scission.

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NEW ELECTRODE MATERIAL: BORON-DOPED DIAMOND COMPACTS

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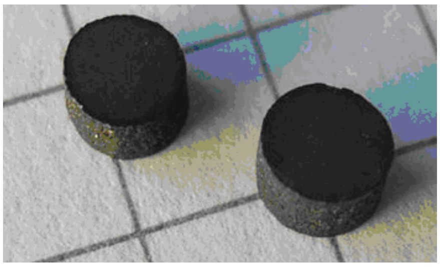

Electrochemical properties of a new electrode material, synthetic diamond compacts with the boron (dopant) level approaching the upper limit, are studied for the first time. Cylinder-shaped polycrystalline samples, 3.5-4 mm in diameter and 2.5 mm in height, were prepared by thermobaric processing of graphite-boron carbide mixtures in the diamond thermodynamic stability region (at the pressure of 8-9 GPa and temperature of ~2500 K) [1]. Their diamond nature, in particular, the absence of graphite, was confirmed by Raman spectroscopy and XRD technique. The compacts' electrode behavior is studied by using cyclic voltammetry and electrochemical impedance spectroscopy. The cyclic voltammograms showed that the compacts are similar to conventional chemical-vapor-deposited thin-film diamond electrodes in their electrode characteristics. In particular, they have wide potential window, low background current in indifferent electrolytes (KCl, K_2SO_4) and good reproducibility. Moreover, their extremely high doping level makes them more electroactive [2]. Thus, the compacts are well comparable to the CVD-diamond electrodes. At the same time, they are free of some drawbacks inherent in the thin-film electrodes (film delamination, thru holes, etc.) One might think that they can equally be used, e.g., as electrodes in electrosynthesis, electroanalysis, water treatment, sensing. At the same time their compact form may be an advantage in the designing of electrochemical devices: sensors, biosensors, etc.

Benzene oxidation at the boron-doped diamond compact anode in 1 M KCl solution is studied by cyclic voltammetry and electrochemical impedance spectroscopy, aiming at elucidation of the role of adsorption processes in the reaction kinetics. The measurements of differential capacitance and anodic current show that some intermediate product of the benzene anodic oxidation adsorbs at the diamond anode and partially blocks it. As a result, both the benzene oxidation and chlorine evolution are hindered. The *f*-sweep и *E*-sweep impedance spectra are measured and analyzed; the intermediate product adsorption was proved by two independent methods [3].

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Photo-renewable engineered sensor based on silica, silver nanoparticles and titania

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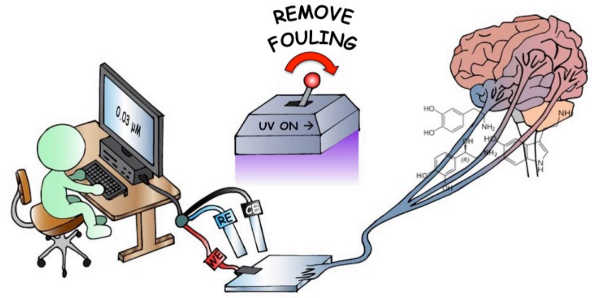
Electrode surface passivation and fouling are important challenges in electroanalysis when using modified electrodes in complex matrices, especially in the biomedical and environmental fields [1-2].

In order to overcome such problems, the production of highly engineered *ad hoc* designed devices could provide really effective sensors [2]. In particular, a reliable and reusable sensor, that could be cleaned by a simple irradiation with UV or solar light, could be perfect for this purpose.

In this context, a three-layered transparent electrode, in which silver nanoparticles are embedded between a bottom silica and a top titania layer is developed [3-4]. Such structure confers to the device multifunctional properties which can be conveniently used in the detection and quantification of some neurotransmitters: dopamine, norepinephrine and serotonin.

The sensor is thoroughly investigated by structural, morphological and electrochemical characterizations in order to understand the role of each component with the aim to improve the robustness and efficiency of the electroanalytical system. In particular, the size distribution of silver nanoparticles, the device architecture and surface homogeneity are inspected by electron microscopy. As confirmed by X-ray diffraction the overlayer is made of anatase (the active polymorph of titanium dioxide), capable of photodegrading model contaminants. Furthermore, electrochemical techniques (cyclic voltammetry and electrochemical impedance spectroscopy) revealed that a highly ordered distribution of silver nanoparticles constitutes the active analytical core of the device, allowing easier electron transfer and better quantification of the analytes.

The system presents good sensing performances, reaching low detection limits even in the presence of typical interferents such as ascorbic and uric acids. Moreover, the titania photoactive top layer allows the complete recovery of the device performance in terms of sensitivity after a fast and simple UV-A cleaning step, affordable with different UV sources. In particular, three lamps (different in terms of power and wavelength) were tested, reaching the total removal of the contaminants in 10-15 minutes [5]. This "self-cleaning" property, combined with a remarkable resistance against aging and ease of use, allows to employ the sensor also for detection in real matrixes, such as liquor and serum.



ACKNOWLEDGEMENTS
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Electrochemistry Provides Better Understanding of Polymer Brushes as Smart Coatings

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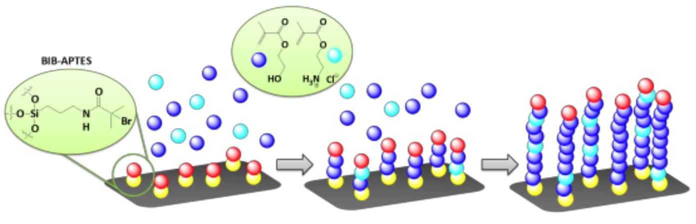
Functional polymer brushes have a tremendous interest for surface engineering, thanks to their stimuli-responsive behavior, allowing applications in the field of switchable wettability/adhesion processes, controlled release and sensor development. However, surface-attached polymer brushes are very difficult to characterize with standard techniques like GPC and NMR due to the very small amount of polymer grafted (~0.01 mg cm^{-2}). Thus, more sophisticated (and expensive) techniques, *i.e.* XPS, are needed in order to achieve a satisfactory knowledge of the sample under study.

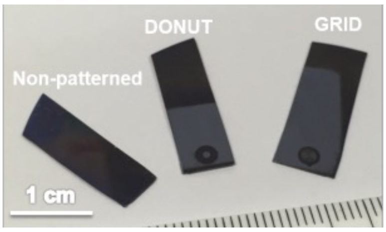
In this work [1] we demonstrate how grafted-from hydrophilic polymer brushes can solve the problem of the development of on-chip electrochemical microsensors, impaired by the electrochemical inertness of native oxide-coated silicon wafer.

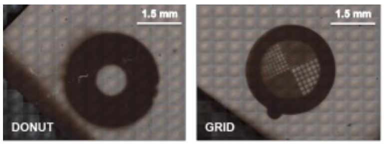
Silicon substrates were functionalized with the alkoxysilane-type BIB-APTES initiator. Polymer brushes with different composition were then grown by SI-ARGET ATRP with different feed ratios of the monomers 2-hydroxyethyl methacrylate (HEMA) and 2-aminoethyl methacrylate hydrochloride (AMA). Both homopolymer (PHEMA, PAMA) and copolymer (PHEMA-*co*-PAMA 80:20, PHEMA-*co*-PAMA 50:50) and micropatterned (by using remote photocatalytic lithography[2]) brushes were obtained and characterized.

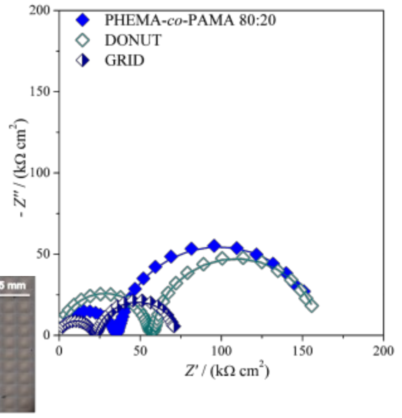
Every step of the grafting procedure, from surface pretreatment to functionalization with initiator and eventually the grafted brushes, was studied using electrochemical techniques, in particular electrochemical impedance spectroscopy (EIS).

In this way, the homogeneity and density of the initiator layer and of the resulting brushes, their composition and thickness and also the post-functionalization reactions could be easily investigated. Brushes with different loading of cationic groups could be differentiated through their marked reactions to an anionic redox probe. Noteworthy, the brushes were grown on silicon substrate which is an atypical electrode material due to its very poor electrochemical response. Grafted-from brushes allowed the reaction of ferrocyanide at the silicon surface, behaving as «tentacles» to capture the redox probe and keep it in proximity of the silicon surface. Micropatterning was found to improve the electrochemical behavior of the system. Our results thus pave the way for the development of on-chip electrochemical devices and sensors. Applications for drug-delivery and microfluidics can be envisaged as well.









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A Sensitive Electrochemiluminescence Immunosensor for Celiac Disease Diagnosis Based on Nanoelectrode Ensembles

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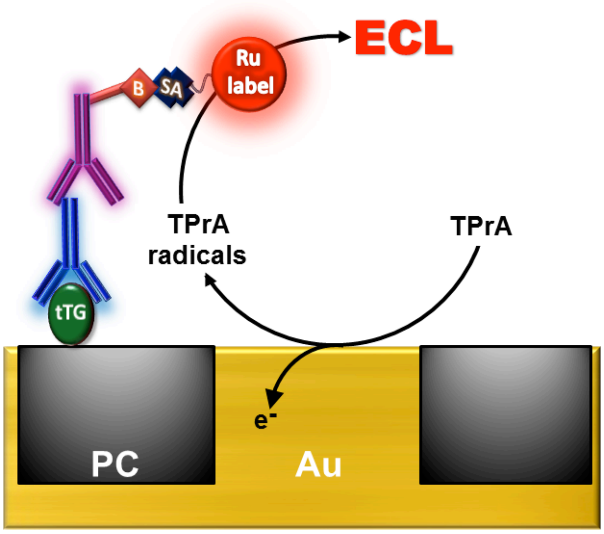
Coeliac disease (CD) is a gluten-dependent autoimmune disorder with a prevalence of 1% in the population. Early diagnosis reduces mortality and prevalence of CD-associated disorders. Research efforts aims at developing tests to detect anti-transglutaminase (anti-tTG) in serum. Electrochemiluminescence (ECL) is the electrochemically initiated emission of light by a luminophore. Systems based on $Ru(bpy)_3^{2+}$ as luminophore and tri-*n*-propylamine (TPrA) as co-reactant are the basis of commercially available ECL immunoassays for cardiac and infectious diseases, tumor markers, *etc*.[1]



We report here the design of a novel immunosensor and its application for celiac disease diagnosis, based on ECL readout, using membrane-templated gold nanoelectrode ensembles (NEEs) as a detection platform.[2] An original sensing strategy is presented by segregating spatially the initial electrochemical reaction and the location of the immobilized biomolecules where ECL is finally emitted.[3] The recognition scaffold is the following:[4] tissue transglutaminase (tTG) is immobilized as a capturing agent on the polycarbonate (PC) surface of the track-etched templating membrane. It captures the target tissue transglutaminase antibody (anti-tTG), and finally allows the immobilization of a streptavidin-modified ruthenium-based ECL label *via* reaction with a suitable biotinylated secondary antibody. The application of an oxidizing potential in a TPrA solution generates an intense and sharp ECL signal, suitable for analytical purposes. The immunosensor provides ECL signals which scale with anti-tTG concentration with a linearity range between 1.5 ng.mL^{-1} and 10 µg.mL^{-1} and a detection limit of 0.5 ng.mL^{-1}. The sensor is finally applied to the analysis of anti-tTG in human serum samples, showing to be suitable to discriminate between healthy and celiac patients.

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Effect of Power Density and Doping on the Electrochemical Properties of Nanocrystalline Carbon (nc-C) Thin Films

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Carbon based electrodes have been extensively used in electrochemical analysis due to their wide potential window, low background current and the large extent to which their structure and surface chemistry can be modified. [1] Nanocrystalline carbon (nc-C) films deposited by unbalanced magnetron sputtering have recently attracted attention because their structure, such as sp^2/sp^3 ratio and crystallinity, can be extensively modified leading to markedly different electrochemical properties [2]. In this study, selected deposition parameters were varied to produce nc-C thin films with different physical structures and surface chemistry, which were then correlated to their electrochemical properties.

Nanocrystalline carbon films with a thickness of 200 nm were deposited on boron-doped Si (100) by close-field unbalanced magnetron sputtering (CFUBM). The power density of the graphite target was varied and the flow rate of H_2, O_2, N_2 gases was carefully controlled during deposition to induce chemical changes to the nc-C films. The films were then characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and elastic recoil detection analysis (ERDA). The electrochemical properties of the nc-C films were investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Several outer-sphere ($Ru(NH_3)_6^{2+/3+}$, FcMeOH) and inner-sphere ($Fe(CN)_6^{4-}$, dopamine) redox couples were used.

The nc-C films deposited with different power densities showed I_D/I_G ratios between 3.2 and 2.8 indicating a high sp^2 content. The electron transfer for $Ru(NH_3)_6^{2+/3+}$ was reversible in the range of power densities used. However, an increase in the peak potential separation (ΔE_p) was observed in the CV measurements for dopamine with decreasing power density. Doping with oxygen and hydrogen greatly affected the electron transfer for outer-sphere redox couples and the ΔE_p values increased with increasing gas flow rate. Similar behavior was observed for the oxidation of dopamine. Doping with nitrogen slightly decreased electron transfer at low flow rates but the electron transfer remained reversible at high flow rates for $Ru(NH_3)_6^{2+/3+}$. EIS results provided further support for the trends observed in the CV measurements.

In conclusion, the structure and surface chemistry of nc-C films can be extensively modified by changing the deposition parameters and these changes are reflected accordingly in the electrochemical properties of the thin films.

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Fabrication of porous Au-Ag bimetallic electrocatalyst synthesized via electrodeposition for CO_2 reduction

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The reduction of carbon dioxide is the promising methods for renewable and sustainable human society. The conversion methods to reusable chemicals have been widely investigated, for example, thermal, photochemical, and electrochemical reduction methods [1]. Particularly, electrochemical reduction method easily controls the product selectivity by changing the electrocatalysts, electrolytes, or reduction potentials of carbon dioxide.

Carbon monoxide, one of the products generated after the electrochemical reduction of carbon dioxide which can be used as the syngas to apply the Fischer-Tropsch process to produce the liquid fuels. Intensive researches on the electrode materials have been reported, since it determines the selectivity and yield of produced carbon monoxide. Among the various metals, Au and Ag is getting attention to produce the carbon monoxide from carbon dioxide [2]. However, Au and Ag are the expensive metal, therefore, the high surface area through modification of morphology of Au or Ag electrode is required to increase the mass activity with low loading amount. Lately, various nanostructured metal electrodes have been investigated for the reduction of carbon dioxide to improve the selectivity and change the composition of product compared to planar metal electrodes [3, 4]. The porous and nanostructured materials can allow the rapid transport of reactants [5]. Thus, extremely high surface area is suitable for electrochemical reduction of carbon dioxide and curved structure could provide a numerous active sites for carbon dioxide reduction [6]. Template-mediated method composed of two steps, 1) synthesis of highly porous template with relatively cheap materials 2) slightly coating Au, Ag, or Au-Ag on the template by electrodeposition, is an efficient way to fabricate catalyst having large surface area.

Herein, the porous dendritic metal electrodes were synthesized by electrodeposition methods. Three-dimensional porous template could be simply obtained with this method by evolving the hydrogen bubbles. And the Au-Ag co-electrodeposition was subsequently performed on the template to modify the surface characterization to enhance the CO selectivity. The selectivity was evaluated in terms of Faradaic efficiency. And the properties of porous electrocatalyst were examined by X-ray diffraction and the field-emission scanning electron microscope.

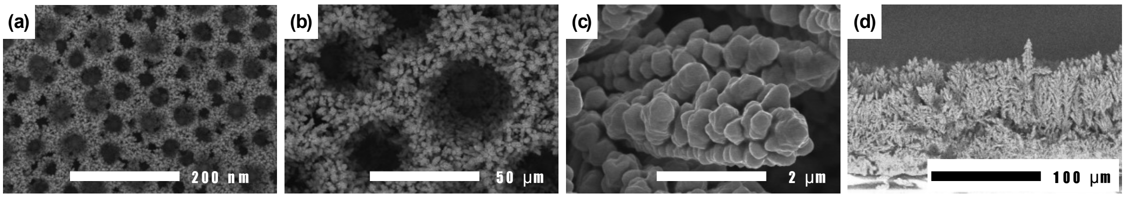

Fig. 1. Porous dendritic metal electrode used as the substrate for co-electrodeposition of Au-Ag bimetallic structure. (a)-(c) surface morphology at different magnifications (d) cross-sectional structure

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Bottom-up Filling of Through Silicon Vias Based on Electrochemically Derived Filling Mechanism With Ammonium-Containing levelers

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Through silicon via (TSV), a vertical interconnection through a silicon wafer, is considered as an emerging technology for the next generation of 3-dimensionally integrated electronic devices. Stacked chips by using TSV shows low power consumption, fast operating speed, and multi-functional performances.

Cu, a typical material used in TSV, is deposited inside the vias by using electrodeposition. Intensive researches have been reported to achieve a void-free filling, because voids formed during the electrodeposition deteriorate the reliability of chips. It is known that selective adsorption of suppressing agents on the top of the via, not on the bottom, is required for the bottom-up growth of Cu [1]. The commonly suggested mechanisms are developed by controlling the additive chemistry, which indicates that the investigation on the behavior of additives must take precedence.

In this study, we synthesize pyridine or choline-based levelers, containing quaternary ammonium salts, to achieve bottom-up filling [2-5]. With the synthesized additives, TSV-scaled trenches (6.5 μm width and 40 μm depth) are galvanostatically filled, under the convective condition to sufficiently supply Cu ion and additives to the electrode surface. As shown in Fig.1, Cu is deposited selectively on the bottom of the via with negligible deposition on the top, which induces the void-free bottom-up filling.

During the filling, different fluidic motions are developed according to the top and the bottom due to the recessed geometry of the trenches; strong convection on the top and stationary flow on the bottom. Electrochemical analyses are conducted at 0 rpm and 900 rpm, to replicate the flow conditions on the bottom and the top, respectively. As shown in Fig. 2, leveler strongly inhibits Cu deposition at 900 rpm while shows negligible inhibition at 0 rpm. Co-added suppressor and leveler maximize the inhibition at 900 rpm, and accelerator more efficiently functions at 0 rpm rather than at 900 rpm when combined with suppressor. Based on the electrochemical results, suppressor and leveler inhibit Cu deposition on the top surface, while accelerator promotes Cu deposition on the bottom, enabling the bottom-up filling.

In conclusion, we will introduce a galvanostatic filling mechanism with considering the effect of additives according to the geometry of the electrode and fluidic motion. The changes in the microstructure of deposited Cu, affected by the functional groups of the adsorbates, are investigated. Furthermore, an improved filling method, step electrodeposition, is proposed to reduce the filling time.

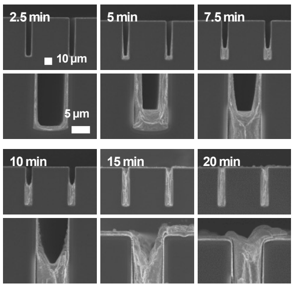

Fig. 1. Filling profiles according to the filling time.

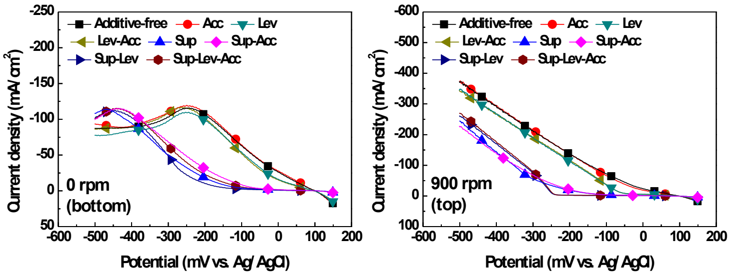

Fig. 2. Voltammograms with differently grouped additives of accelerator (Acc), suppressor (Sup), and leveler (Lev).

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Effect of emulsified binders on the performance of carbon electrochemical double-layer capacitors

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In recent years, much attention on powerful energy storage devices such as lithium ion batteries and supercapacitors have been paid due to their high energy density and high rate capability. The supercapacitors such as electrochemical double-layer capacitor (EDLC) showed various application, especially to the field of high-rate charge/discharge because they store energy in a physical manner. So far, tremendous research on their electrode materials and electrolytes have been done whereas little attention has been give to polymer binder providing electrical network structure by holing electrode materials together with current collector.

In this study, two emulsified polymers are used to compare their electrochemical performance on EDLC using activated carbons; styrene-butadiene rubber (SBR) and polytetrafluoroethylene (PTFE). These are conventional binder materials used for EDLCs. A variety of physical and electrochemical characterization techniques are applied to explain the effect of the ratio of the two emulsified binders on EDLC performance.

A Label-Free, Sensitive, Real-Time, Semiquantitative Electrochemical Measurement Method for DNA Polymerase Amplification (ePCR)

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Described in here is a novel method for label free, electrochemical, real time detection of the polymerize chain reaction (PCR) by using electrochemically conducting polymers (ECPs). Oligonucleotide hybridization to a complementary sequence that is covalently attached to an ECP coating the working electrode of an electrochemical cell causes an increase in reaction impedance for the ferro-ferricyanide redox couple. We demonstrate the use of this effect to measure, in real time, the progress of DNA polymerase chain reaction (PCR) amplification of a minor component of a DNA extract. The forward primer is attached to the ECP. The solution contains other PCR components and the redox couple. Each cycle of amplification gives an easily measurable impedance increase. Target concentration can be estimated by cycle count to reach threshold impedance. As proof of principle, we demonstrate an electrochemical real-time quantitative PCR (e-PCR) measurement in the total DNA extracted from chicken blood of an 844 base pair region of the mitochondrial Cytochrome c oxidase gene, present at □1 ppm of total DNA. We show that the detection and semiquantitation of as few as 2 copies/µL of target can be achieved within less than 10 PCR cycles.

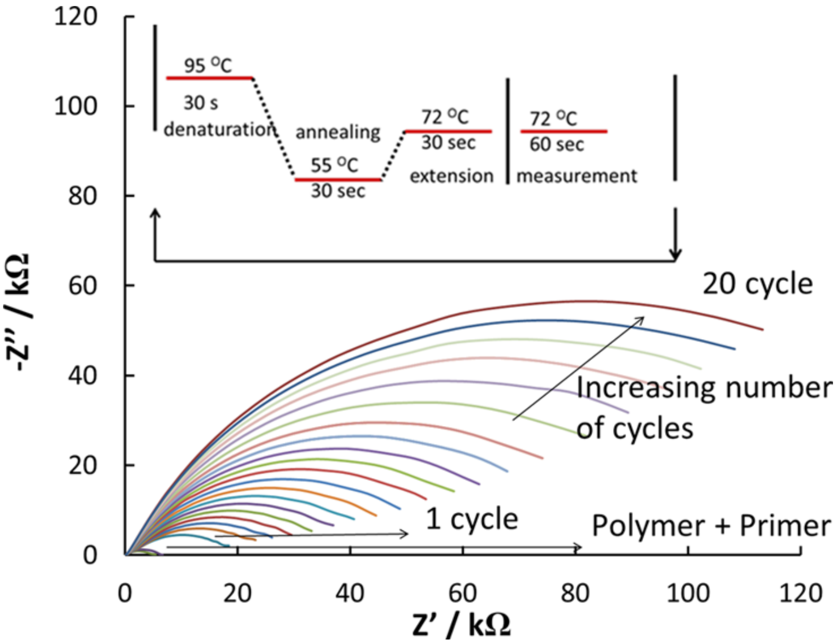

Figure : Evolution of EIS signal with increasing number of PCR cycles due to the surface located DN amplification as well as hybridization of solution amplified DNA to the forward primer.

Electrochemical and Surface Analyses of Acrylic – Silicone - NanoSio$_2$ Based Nanocomposite Corrosion Protection Coatings

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Development of corrosion protection coatings utilizes the incorporation of nanomaterials to enhance the electrochemical and surface properties. In this study, the influence of SiO_2 nanoparticles in improving the hydrophobicity and the corrosion protection capability of hybrid acrylic-silicone polymeric matrix was investigated. Contact angle measurements (CA) has been carried out to evaluate the wettability of the developed coated surfaces. Electrochemical impedance spectroscopy (EIS), Tafel test and salt spray tests are prominent techniques to determine the corrosion protection performance of all developed nanocomposite coating (NCs) systems. The morphology and the topography of the developed nanocomposite coatings have been deeply analyzed by atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDX). Electrochemical analyses show that the system with 3 wt. % SiO_2, AS 3, possesses significant corrosion protection ability by showing coating resistance in the range of 10^9 ohm even after 90 days of immersion in electrolyte solution. The contact angle of this system was found to be maximum as 97.3°. The morphology and topography studies clarify the influence of nano-sized SiO_2 filler on the surface topography and demonstrated the uniform and proper distribution of the embedded SiO_2 nanoparticles within the acrylic – silicone polymeric matrix.

Keywords: corrosion, silicone, acrylic resin, salt spray test, EIS, nanocomposite coatings

Mixed diazonium/PEDOT-functionalized graphene electrode for antioxidant biomarkers detection: proof-of-concept for integration on silicon substrate

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During the last two decades, a growing number of research works has been devoted to oxidative stress, which represents a major problem with respect to healthiness, as it is known to be involved in ageing processes and has been suggested to be one of the potential causes for cataract, cancers, cardiovascular and degenerative diseases (Parkinson, Alzheimer) and even male infertility [1]. Among the low molecular weight antioxidant species, ascorbic (AA) and uric (UA) acids are of particular interest since they are present in most biological fluids and thus may be considered as biochemical markers in a lot of pathologies related to oxidative stress (preeclampsia disease, neonatal hypoxia, coronary heart diseases…) [2].

Recently, we have reported on a sensor based on a gold electrode functionalized by an electrogenerated polymer, namely poly[3,4-ethylenedioxythiophene] (PEDOT), for the simultaneous assay of UA and AA [3-5]. This sensor exhibited very good analytical performances including selectivity. We further improved the sensor by using a glassy carbon (GC) electrode functionalized by successive electrodeposition of 4-thiophenylbenzene diazonium (TBD) and (PEDOT) [6]. The use of the TBD layer induced an enhancement of the sensitivity, a lower detection limit for AA and an improved lifetime of the sensor. However, GC is hardly compatible with the silicon technologies required for a cost-effective mass production of integrated microelectrodes and the associated electrochemical microcells.

In the present work, we have developed the proof-of-concept of a mixed TBD/ PEDOT functionalized graphene electrode integrated on a silicon substrate for the simultaneous detection and assay of UA and AA. The catalytic chemical vapour deposition (CVD) synthesis of graphene on either platinum (Pt) foils or thin films will be detailed, together with its electrochemical functionalization by both TBD salt grafting and EDOT electropolymerization. The characterization of the resulting modified electrodes by Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and cyclic voltammetry (CV) will be presented. The analytical performances obtained for AA and UA detection and quantification will be also discussed, and a focus will be given to graphene advantages over GC in terms of selectivity and sensitivity.

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Effect of Surface Pretreatment of Dimensionally Stable Anodes on the Performance of the Anodic Reactions

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Recent wastewaters from food, textile or other industries contains highly anti-oxidative organic matters which is hardly oxidized by conventional wastewater treatment processes. The electrochemical treatments are good at the pretreatment of the aforementioned organic compounds as an advanced oxidation process (AOP). It are greatly dependent upon the specific water quality matrix of the wastewater for chemical AOPs, but the electrochemical treatments, especially, electrochemical oxidations using dimensional stable anodes (DSAs) are broadly applicable. Even though main objectives of most of AOPs are direct oxidation of non-biodegradable organic matter, it might cause an increase in the difficulty in optimizing operation parameters or non-selectivity for target organic matter due to the formation of by-products. To overcome those disadvantages, in this study DSAs for electrochemical oxidation reactions was introduced to convert highly anti-oxidative organic matters into biodegradable ones. Many parameters for improved anodic reactions should be optimized, but in this study the surface pretreatment of bare titanium electrodes prior to the specific metals (e.g., Ir, Ru, Pt, etc) coating on DSAs was focused to increase the performance of anodic reactions. The removal of oxide layers and the roughness of the surface of bare titanium plate electrodes were controlled by acid treatment and polishing, respectively. They significantly affected the performance of anodic processes. It was confirmed in terms of SEM, XRD, various voltammetry methods, electrochemical impedance spectroscopy, and accelerated life tests.

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Determination of Food Dyes in Soft Drinks Using MWCNT-modified GCE

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Food colorants are substances added to food and soft drinks during their manufacture or processing. They are used for compensating the loss of natural colors and with the aim of enhancing the aesthetic appeal of foodstuff to the consumer. However, some of these chemicals represent a potential risk to human health, especially if they are excessively consumed[1,2]. Their reduction mechanism is well known[3] unlike its electrooxidation which changes according to the type of electrode and the nanomaterial used as modified[4–6]. On the other hand, multiwalled carbon nanotubes (MWCNT) has been used as electrode material for the determination of different analytes[6,7]. The main problem associated to MWCNT is to get homogeneous dispersions. This problem was solved by using 1,3-dioxolane a green solvent that is nontoxic, odorless, environmentally friendly and produced nanotube dispersions that leave no residues on electrodes when it evaporates[8].

Because of this, the aim of this work is to study the electrooxidation of food dyes onto MWCNT-modified glassy carbon electrode (MWCNT/GCE) and quantify them in soft drinks used in Chile.

The electrochemical behavior of tartrazine (TZ), sunset yellow (SY), carmoisine (CR) and allura red AC (AR) was studied by cyclic voltammetry and differential pulse voltammetry. The influence of scan rate, accumulation time, MWCNT concentration and pH is discussed.

At GCE the oxidation of these colorants is pH dependent, irreversible for TZ, AR and CR and EC_{irrev} for SY. At MWCNT-modified GCE the oxidation of these colorants remains pH-dependent but changes in the cyclic voltammetric profiles and the electrooxidation mechanism were observed.

By differential pulse voltammetry, all food dyes exhibiting a well-defined oxidation peaks at pH 7.0. Under the optimal conditions, the limit of detection and quantification and repeatability were calculated, following the oxidation signal of each colorant. The results show an improvement of the analytical response when MWCNT was used, enhancing the sensitivity of the electrodes. Finally, the application of this electrode was demonstrated by measuring food dyes in soft drinks samples commercialized in Chile. The results were compared with High Performance Liquid Chromatography (HPLC). The concentrations obtained with MWCNT/GCE are in agreement with HPLC but the acquired time of analysis is improved.

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Electrochemical Deposition of Mixed Metal Systems and Their Electrocatalytic Properties

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The electrochemical formation of nanostructured materials has received significant attention due to their interesting electronic, optical and catalytic properties. The ability to change the size, shape and composition of a material is of particular interest given that control over these properties allows one to tailor design a nanomaterial with a specific catalytic reaction in mind. The advantage of an electrochemical approach is that is generally facile, rapid and results in well adhered materials to the underlying support which is extremely critical to the formation of an effective electrocatalyst.

In this work the electrodeposition of bimetallic and trimetallic systems based on Co/Au and Co/Ni/Fe is explored under various conditions such as precursor salt concentration, applied potential and time and how this influences composition, morphology and crystallinity of the final materials. In particular the formation of amorphous metal hydroxide materials was found to be highly desirable. They are then investigated for technologically important electrocatalytic reactions such as the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) where in some cases a dual action catalyst was fabricated that was highly active for both reactions. In addition enhanced performance for the OER in terms of current density, overpotential and long term stability compared to commercial IrOx was achieved under alkaline conditions.

This approach in principle can be utilized to generate a wide range of nanostructured materials that are active for both the OER and ORR reactions and gives insights into the role that surface chemistry and crystallinity play for such important reactions.

In-Situ Polymerization of Poly(acrylonitrile-butylacrylate)-Graphene Nanocomposite as a Promising Water-Based Binder for High Performance Lithium-ion Batteries

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Nowadays, due to graphene (GP)'s preeminent characteristics, it has been widely used in many different areas. In polymer nanocomposites, it is believed that graphene is one of the extraordinary fillers related to its very good mechanical properties, remarkable electron mobility and heat conductivity. In our previous study, we reported an efficient, promising water-based binder, poly(acrylonitrile-butylacrylate) (P(AN-BA)), for negative electrodes of lithium-ion batteries (LIBs). In this work, by the addition of GP to the polymerization of P(AN-BA) via in-situ polymerization technique, we'd like to introduce a new P(AN-BA)-GP nanocomposite which is very well-dispersed, water-based as well as high performance binder for LIBs, especially high capacity LIBs. Different amounts of GP had been tested to find out the optimum value and the final products were physical and electrochemical characterized then compared with either solution mixing P(AN-BA)-GP or commercialized styrene-butadiene-rubber (SBR) water-based binder.

Definition of Important Issues in Passivity Breakdown

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In order to develop deterministic models and algorithms for predicting the development of localized corrosion damage in industrial and aerospace systems, due to pitting attack and subsequent stress corrosion cracking/corrosion fatigue, we are refining the mechanisms for passivity breakdown and the nucleation of meta-stable pits within the framework of the Point Defect Model (PDM). Since passivity breakdown is the initial event that occurs in the accumulation of localized corrosion damage, it is critically-important that highly deterministic models be developed to describe this process in nanoscopic detail. Our objective is to identify critical parameters in the model that are difficult to directly measure experimentally, but which may be determined by using "first principles", quantum mechanical and molecular dynamics techniques, which are being developed elsewhere in this program. In this paper, the basis of these methods will be reviewed within the framework of our present understanding of the mechanisms of passivity breakdown on iron, stainless steels, and aluminum alloys, with emphasis on the nature of the breakdown site and the processes involved in the breakdown event at the atomic level. It is argued, upon the basis of experimental evidence, primarily for aluminum, that passivity breakdown occurs via the condensation of cation vacancies at the metal/barrier interface of the barrier layer of the passive film. Cation vacancy condensation occurs because the absorption of chloride ions into oxygen vacancies in the surface of the barrier layer, resulting in an enhanced flux of cation vacancies across the barrier layer. If these vacancies cannot be annihilated at the m/bl interface via injection of a cation from the metal, the excess vacancies condense to form the condensate blisters that are the precursors to passivity breakdown, as has been reported experimentally. This mechanism accounts quantitatively for the pit nucleation rate versus time, which is observed to pass through a maximum. A blister is observed to grow with time, which we attribute to continued condensation of vacancies at the periphery until the blister fractures and nucleates a metastable pit, if the pit nucleus cannot establish differential aeration. This model predicts that the radius of the blister increases with time, while simultaneously thinning due to dissolution of the barrier layer at the barrier layer/porous outer layer interface. This model accounts for all of the experimental data of which the authors are aware on passivity breakdown and the nucleation of metastable pits on aluminum alloys.

Surface Modification Strategies for Silicon Anodes towards Very Robust Cycling upon Deep Lithiation

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Pulverization of electrode materials and loss of electrical contact have been identified as the main causes for the performance deterioration of alloy anodes. In this talk, we describe the hierarchical arrangement of spatially confining silicon nanocrystals within several different physical insulting capsules for alleviating these issues. Firstly, an elastic, highly oriented graphene monolith was engineered to fully encapsulate the silicon nanoparticles, serving as a robust framework with the well-accessible thoroughfares for electrolyte percolation, as well as an electrolyte blocking layer to restrain Si from direct exposure to electrolyte without sacrificing the high-efficiency electron/Li ion transport channels; in return, the pillar effect of Si NPs prevents the graphene sheets from re-stacking. Secondly, we also attempted to develop a F-doped TiO_{2-x} layer on the silicon surface with additional possibility of the in-situ etching of the native oxide layer into a hollow interior. When evaluated as binder-free anodes, both type of the electrodes exhibit a remarkable cycle life for more than 1000 cycles with average coulombic efficiency higher than 99.5%. Operando XRD and synchrotron-based XPS confirmed the formation of the most volume expanded lithiated phase $Li_{15}Si_4$, suggesting the effective buffering of the volume variation upon cycling. Furthermore, we also develop a GF/Si free-standing film through re-adjusting the pore size in GF/Si monolith. Thanks to electrical conductivity, the elasticity and structural integrity of GF monoliths, the as-developed GF/Si free-standing film showcases the potential use in the flexible electronic devices.

The Role of Quantum Mechanics in Determining Corrosion Phenomena

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Beginning with the work of Gurney in the 1920s, which was communicated to the Royal Society by Lord Rutherford of Nelson, and expanded upon later by Gerischer, Schultze, and Marcus, amongst others, the kinetics of charge transfer reactions, particularly on passive metal surfaces, have contained a quantum mechanical tunneling (QMT) component to account for the transfer of charge carriers across the barrier layer of the passive film or to the inner Helmholtz plane where the initial state of a charge transfer reaction is envisaged to reside on a film-free metal surface. In the case of passive metals, the impact of QMT on the kinetics of a charge transfer reaction is clearly defined in terms of the tunneling probability of the iso-energetic transfer of charge carriers from filled electronic states in the metal to empty electronic states in the reactant, which may be calculated from first principles by solving Schrödinger's equation as initially described by Gurney. In this presentation, we apply quantum mechanical principles to acquire a more accurate definition of the impact of QMT on corrosion processes, primarily through the probability of the tunneling of charge carriers through the barrier layer on a passive metal. We illustrate the impact of QMT with respect to the corrosion of carbon steel in alkaline environments under highly anoxic environments, the establishment of the corrosion potential of stainless steel in boiling water (nuclear) reactors (BWRs), and on the stress corrosion cracking of stainless steel in the same environment. By applying QMT principles, it is possible to assign an exchange current density to the film-free surface, even though such a surface may be hypothetical in nature (i.e., a film-free surface may not be achievable in practice), and to account for the impact of the barrier layer on corrosion phenomena as the thickness of the barrier layer changes with the corrosion potential. It is shown that a single film-free exchange current density suffices to account for the corrosion potential and corrosion kinetics in these systems.

The Electrochemical Behaviour of Trinitrotoluene (TNT) 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 stability[1] – 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 EC_2 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.

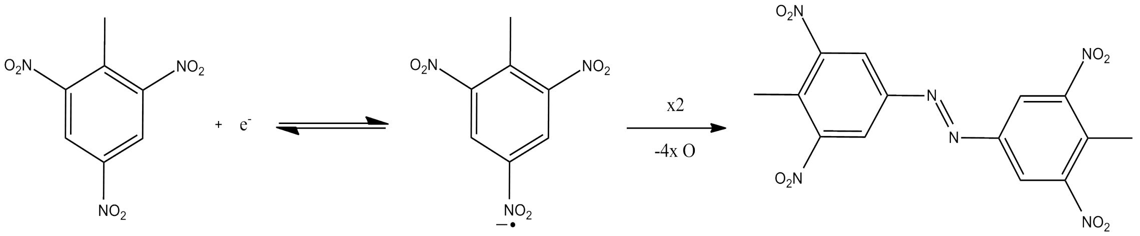

Figure 1: Proposed scheme of the EC_2 mechanism of TNT reduction, forming one of the possible electrogenerated azo products.

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Is Catalyst-Support Interface Necessary for Oxygen Reduction Reaction on TiN-Core Covered with Nitrogen-Doped Rutile-Shell Catalysts?

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The oxygen reduction reaction (ORR) is sluggish at the operating temperatures of many metal-air batteries and fuel cells, including acidic polymer electrolyte fuel cells (PEFCs) for vehicles. Extensive efforts have been made to reduce the usage of platinum-group-metals (PGMs) that catalyze ORR at the cathodes. Although the PGM loading at PEFC cathodes has been reduced five-fold since 2005, further reduction or development of non-PGM catalysts is needed to put PEFCs into global vehicle markets [1,2].

Natural abundance is one of the key attributes of non-PGM catalysts used in PEFC cathodes. Most of the non-PGM catalysts developed in the last decade contain iron, carbon, and nitrogen [2] or sulfur atoms [3] because of these elements' abundances and high activities. We focused on another type of non-PGM catalyst—TiO_2 compounds—because they are (1) insoluble in 0.1-mol dm^{-3} H_2SO_4 at 50°C for 24 days and are therefore stable in PEFC environments [4]; (2) amenable to the incorporation of oxygen defects, which have been acknowledged as ORR active sites [5]; and (3) abundant in nature. The oxygen defects have been incorporated into oxide catalysts using various routes such as the pyrolysis under reductive atmosphere containing hydrogen [4], so-called carbothermal-reduction [6] and nitrogen-doping [7-10]. In case of defect-incorporated TiO_2, rutile is more active for ORR than anatase [5,8,9], different from the trend in photocatalytic activity.

In this work, the ORR-active nitrogen-doped rutile catalysts were synthesized on the surface of conductive TiN to form core-shell structure using a previously reported solution phase combustion route [9,10]. Except for Ta_3N_5 [11], most of the transition metal nitrides including TiN are known to be unstable or even dissolved in acidic media. However, the nitrogen-doped rutile shell on TiN-core retained the ORR mechanism in O_2-purged 0.1 mol dm^{-3} H_2SO_4 solution after 20,000 potential cycles between 0.6 and 1.0 V versus the reversible hydrogen electrode. Further, the activity has been enhanced by changing the supports from carbon black to conductive oxide or even without using supports. Their active sites and the effect of catalyst-support interface on the activity will be discussed at the meeting.

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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 functionalize 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 characterization 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 a 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 sheet. It also provides insight into the electrochemical properties of such systems.

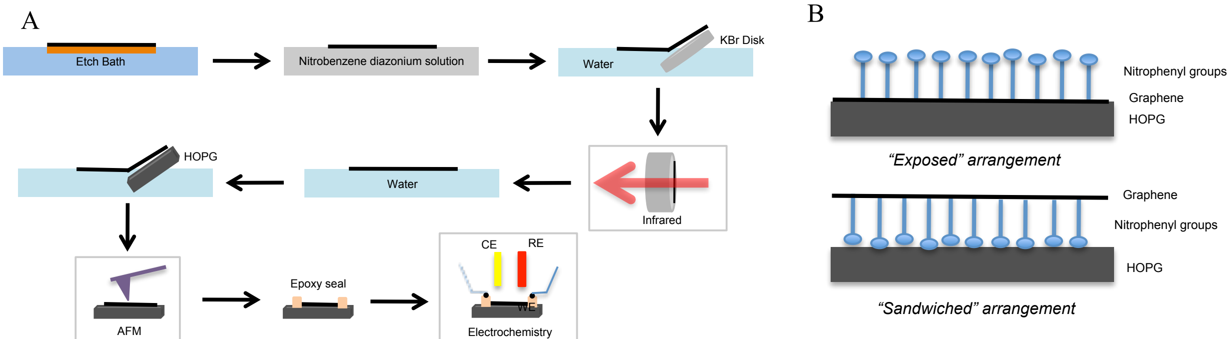

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Figure 1: (A) Novel protocol for the modification and subsequent analysis of free-floating, few-layer graphene; (B) "Exposed" vs. "Sandwiched" arrangement for electrochemistry

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Modifying Graphene via the Diels-Alder Reaction of an Anthranilic Acid: New Chemistry for Graphene Energy Storage Materials

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The development of a sustainable future for energy is of paramount importance. This includes developing both renewable energy sources and energy storage devices. The outstanding electronic, mechanical, and thermal properties of graphene, along with its extraordinarily large surface area mean it has significant potential as a supercapacitor material. In order to construct workable capacitance devices from graphene it is first necessary to covalently functionalize graphene sheets. This will both improve ease of handling,[1] and provide an opportunity to increase the capacitance of the sheets by introducing defects.[2]

This work explores a novel method for the divalent functionalisation of few-layer graphene. The reaction involves a Diels-Alder cycloaddition of an aryne, generated from an anthranilic acid precursor, to the few-layer graphene sheet. This method is expected to preferentially modify the basal plane of graphene. The films have been characterized by infrared and Raman spectroscopy, atomic force microscopy, and electrochemistry. The electrochemical results indicate that altering either the reaction time or the concentration of anthranilic acid in the reaction mixture can effectively control the surface concentration. Electrochemical impedance spectroscopy and cyclic voltammetry have been used to measure both the differential and integral capacitance of these systems.

This work outlines a novel protocol for the controllable and preferential modification of the basal plane of few-layer graphene sheets. It also begins to explore the energy storage capacity of such systems.

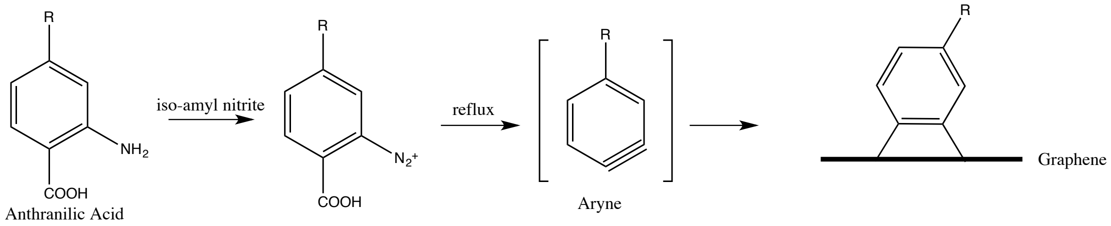

Figure 1: Generation of an aryne, followed by divalent functionalisation of few-layer graphene

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Electrochemistry of Pyridoxine (Vitamin B_6) in Acetonitrile

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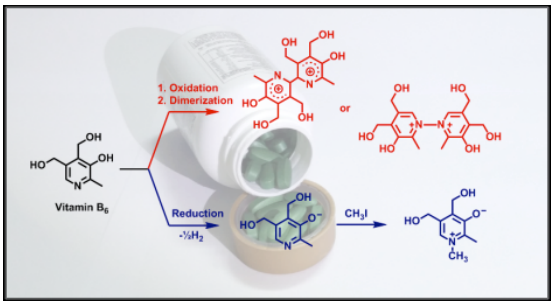

As an important micronutrient, vitamin B_6 (VB_6) has participated in over 100 enzyme-catalyzed reactions in the human biological system. Among the six vitamers present in the VB_6 family, pyridoxine (PN) was the first to be discovered and has since been used frequently in vitamin supplements and in food fortification because of its superior stability. To date, majority of the electrochemical works have been directed to the detection and quantification of PN, while information regarding its mechanistic pathways remains uncertain.[1,2] In addition, most of these reports were conducted using in aqueous media. As aprotic solvents can sometimes aid in improving the lifetimes of reactive species, the present study was examined in acetonitrile with the aim of identifying intermediates produced during the oxidation and reduction of PN. It was found that in acetonitrile, PN can undergo both electrochemical oxidation and reduction independently. The anodic process appears to be chemically irreversible and fouled the electrode surface. Therefore, preparative scale oxidation was performed using a chemical oxidant, $NOSbF_6$, and a dimeric product was suggested to be formed. In contrast, the reduction process was observed to be chemically reversible only on the shorter timeframe of a few seconds but not over prolong period of electrolysis timescale. The cathodic process was proposed to proceed via a direct discharge of PN, generating an oxide anion which after treatment with iodomethane, afforded an N-methylated PN.

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Primary Colored Electrochromism of 1,4-Phenylenediamines

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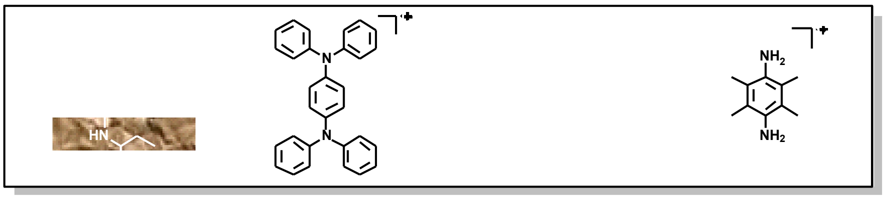

Following an electron-transfer reaction, the light absorption characteristics of electrochromic materials often transition significantly and reversibly.[1] More specifically, the absorption bands of these substances usually change between the UV region (colorless) to the visible region (colored) when they undergo a redox reaction.[1] This property has facilitated numerous commercial applications including electrochromic displays, "smart" windows, and glare-reduction mirrors.[1] We had previously reported that the one-electron electrochemical reduction of aromatic oxygen and sulfur para-diesters gave vivid color changes from an initial colorless state in their neutral forms.[2] In the present study, ten easily accessible and structurally varied 1,4-phenylenediamines were studied in CH_3CN using voltammetric and chronoamperometric techniques in conjunction with UV-Vis spectroscopy. Overall, it was found that one-electron oxidation of the aforementioned compounds produced vibrant colored radical cations that appeared to be relatively unaffected by atmospheric oxygen or moisture. The use of a gold micro-mesh electrode, laminated inside a polymer film to examine the electrochromic properties of four of the 1,4-phenylenediamines (selected to represent the colors red, green, blue, and yellow) is also discussed. Lastly, the colored radical cations of these four electrochromes were monitored for color retention over a period of 24 hours, as well as characterized by electron paramagnetic resonance spectroscopy.

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Electrochemical properties of fluorinated activated carbon for supercapacitors

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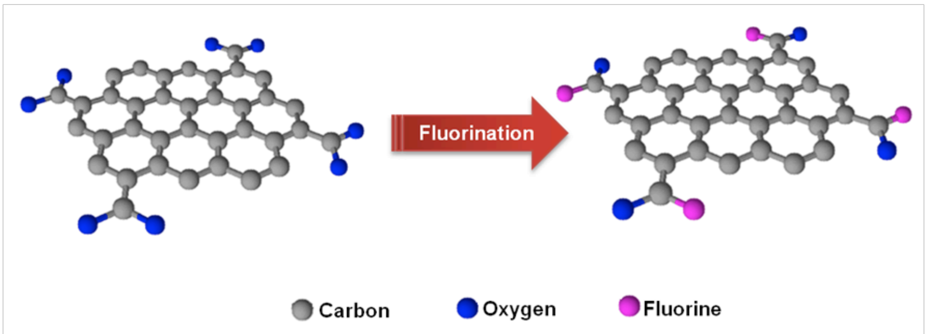
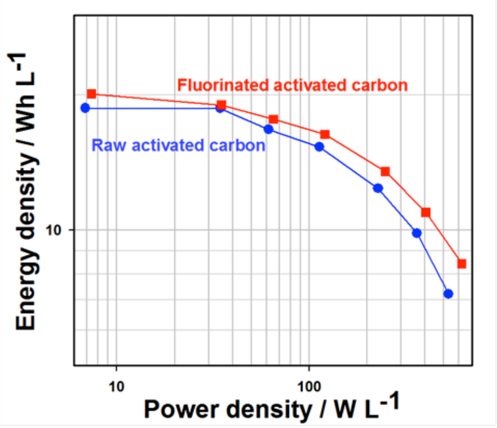
Fluorinated activated carbon (F-AC) is effectively improves the electrochemical capacitive performance compared to raw activated carbon (R-AC). F-AC electrode shows a specific capacitance coming up to 19.8 F cm^{-3}, whereas the capacitance of R-AC electrode is 18.4 F cm^{-3}. Besides, the kinetic enhancement of F-AC is also memorable. This phenomenon indicates that F-AC tends to form electric double-layer ions on its surface more rapidly than does R-AC. This formation is a result of the increased electrical conductivity attributed to the semi-ionic bonding character between fluorine and activated carbon. The electrochemical improvement of F-AC proves that fluorination is a very effective method for providing greater possibilities for supercapacitor applications of AC in nonaqueous electrolytes.





Metal Nanoparticles Decorated Polyaniline-Nanocrystalline Zeolite Nanocomposite Based Electrochemical Sensors for the Nanomolar Detection of Environmental Water Pollutants

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Abstract: *Metal nanoparticles decorated polyaniline-nanocrystalline zeolite nanocomposite materials were synthesized and investigated in the electrochemical detection of environmental water pollutants (lindane, hydrazine, and phenylhydrazine).*

1. Introduction

Among the nanoporous materials, zeolites are currently being used in the wide range of sustainable industrial processes.[1] In this presentation, synthesis, physico-chemical characterization of metal nanoparticles decorated polyaniline-nanocrystalline zeolite nanocomposite (M-PANI-Nano-ZSM-5; M = silver or copper) and their application in electrochemical detection of environmental water pollutants will be discussed.

2. Experimental

Nanocrystalline zeolite was hydrothermally synthesized by our own reported procedure.[2] PANI-Nano-ZSM-5 hybrid material was synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate (APS) in an aqueous zeolite suspension by the in-situ surface polymerization method. Highly dispersed metal nanoparticles were then supported on the nanocomposite material.

3. Result and discussion

The results demonstrate that silver nanoparticles decorated PANI-Nano-ZSM-5 exhibited high electrocatalytic activity for the electrochemical detection of lindane, whereas, copper nanoparticles decorated PANI-Nano-ZSM-5 exhibited high electrocatalytic activity for the determination of hydrazine and phenylhydrazine (Fig. 1).

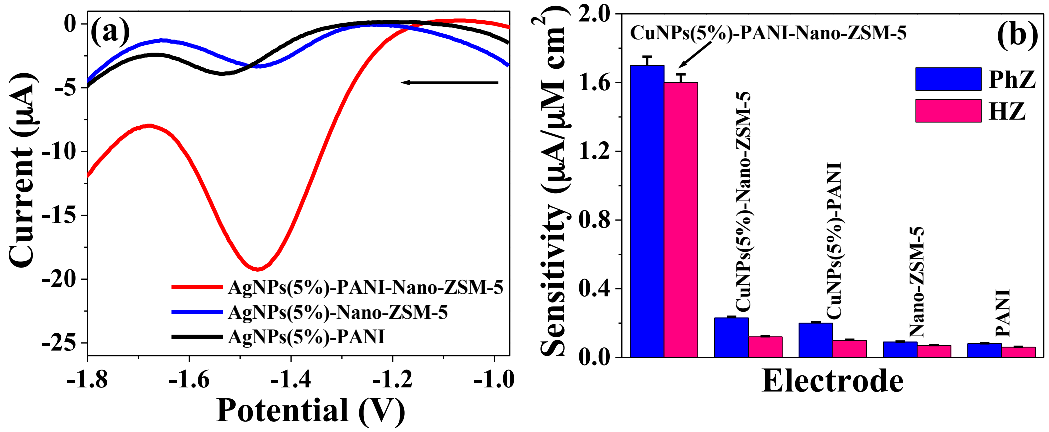

Fig.1. Comparison of (a) DPVs towards lindane reduction and (b) sensitivity towards electrochemical oxidation of phenylhydrazine (PhZ) and hydrazine (HZ) at various modified electrodes investigated in this study.

4. Conclusion

The proposed methodology is simple, rapid and provides a potentially new analytical platform for the detection of environmental water pollutants.

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Solid Phase Extraction - Voltammetric Coupled Detection of Caffeine in Acetonitrile

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Previous electrochemical detection of caffeine (CAF) in aqueous sample solutions were mostly performed directly in the diluted sample solution using modified electrodes. While low detection limit can be obtained with such electrodes, electrode pre-treatment step might be required. Furthermore, any compounds present in the sample solutions that might foul the electrode or have oxidation potential similar to CAF could interfere with the detection of CAF. A recent study found that CAF could undergo one electron oxidation in acetonitrile.[1] Therefore, CAF in aqueous sample solutions was extracted into acetonitrile using solid phase extraction (SPE) before electrochemical detection. The voltammetric detection of CAF in acetonitrile was performed in a microcentrifuge tube after SPE to minimise the solvent and reagents used during analysis. The results obtained from voltammetric determination on a range of beverages extracted into acetonitrile was in good agreement with the measurements obtained from HPLC. The SPE-coupled voltammetric detection gave better results compared to direct voltammetric detection on the bare electrode.

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Influence of Magnetic Field on Interface Electrochemistry of Nickel-based Organic Coating

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With the development of marine economy, electromagnetic shielding coatings (EMSC) have been widely utilized in offshore facilities such as ships and oil field platforms. Commonly, researchers most likely focused on the improvement of the functionality of EMSC, i.e. EMS effect, and few reports revealed the influence of the service condition on the corrosion resistance of EMSC. In this article, the electrochemical behavior of nickel-based electromagnetic shielding coating was studied in 3.5% NaCl solution coupled with a vertical magnetic field of 0.1T. In addition, a vanish coating was investigated as a contrast. Based on that, the effect of magnetic field on the interface electrochemistry of the coating system was analyzed with the aid of Electrochemical Impedance Spectroscopy (EIS) and equivalent electrical circuits models. Commonly speaking, EMSC was not expected to exhibit a good corrosion resistance because the addition of Ni particles might generate more defects in the resin system. It was verified by EIS results, in which the impedance magnitude of the coating at a frequency of 0.01Hz ($|Z|_{0.01\mathrm{Hz}}$) was 10^4 $\Omega\cdot\mathrm{cm}^2$ at the initial stage of immersion, and it decreased to 10^3 $\Omega\cdot\mathrm{cm}^2$ after 4 h immersion. According to the simulation of equivalent circuit, the electrolyte solution already arrived at the coating/ metal substrate interface at this moment. Then Fe-Ni galvanic couple was formed, further accelerating the electrochemical reaction at the substrate. Differently, $|Z|_{0.01\mathrm{Hz}}$ of the same type of samples increased to 10^5 after 1h immersion in the magnetic field and did not decline until the fourth day of immersion. Meanwhile, a transition from two time constants to one time constant could be recognized in Bode diagram versus immersion time during the first three days, which indicated the application of magnetic field could hinder some electrochemical process during the corrosion procedure of EMSC. On the contrary, the varnish coating manifested a faster corrosion rate when the magnetic field was applied to it. The above two difference could be attributed to the movement of ions or particles resulting from magnetic field force during the corrosion processes of coatings. 1) With the application of magnetic field, magnetic force could be generated between adjacent Ni particles, causing the movement of particles in the resin. This led to a better dispersion of Ni particles and a less porosity of coating, as verified by SEM microphotographs, which blocked or prolonged the diffusion path of electrolyte at filler/resin interfaces and somewhat hindered the electrochemical reaction at the coating/metal interface. This effect was predominant when the electrolyte only migrated in the resin. 2) The effect of Lorentz force on ions accelerated the horizontal diffusion of the solution in the coating, and promoted the electrochemical process, which was determinative after the electrolyte reached the interface between coating and metal substrate role .

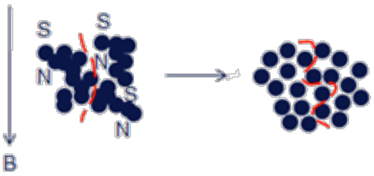
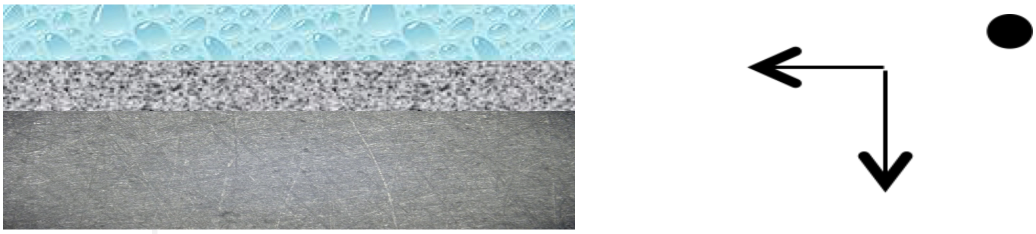


Fig.1 The effect of the vertical magnetic field on filler dispersion (the red lines indicate the diffusion path of electrolyte)



(a) schematic diagram of electrolyte diffusion (b) the Lorentz force

Fig.2 The effect of the vertical magnetic field on electrolyte diffusion in the coating

A Novel Platinum-modified Titanium Electrode for Electrochemical Ozone Generation Prepared by the Multiple Electrostrike Method

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There are some electrodes for electrochemical ozone generation. For example, boron-doped diamond (BDD) electrode [1] and tantalum oxide–platinum composite electrode [2]. However, these electrodes cannot be prepared with low cost, large area, and simple methods. In this work, electrochemical ozone generation at an easily prepared platinum-modified titanium (Pt/Ti) electrode was investigated in comparison with a BDD or a Pt electrodes. The Pt/Ti electrode was prepared by our original method, multiple electrostrike (ME) method as follows. A vibrating Pt wire (cathode) was rubbing over the titanium plate (anode) surface with 7.5 V of potential. Molten Pt metal were sprayed onto Ti plate with several μm sizes. Ozone generation activity of the electrodes were evaluated in acryl sealed 36 L box (Fig. 1 left). Ozone gas has been generated potentiostatically (5 V) in 3 mL of 0.5 M H_2SO_4 and dispersed by the fan. Ozone generation activity of the Pt/Ti electrode was found to be much higher than that of a BDD or a Pt electrodes (Fig. 1 right). The superiority of the Pt/Ti electrode over simple preparation method, in terms of the flexibility, durability, and ozone generation activity were demonstrated with the conventional methods and conditions. This research is attractive to develop a practical unit for inexpensive and effective ozone generators.

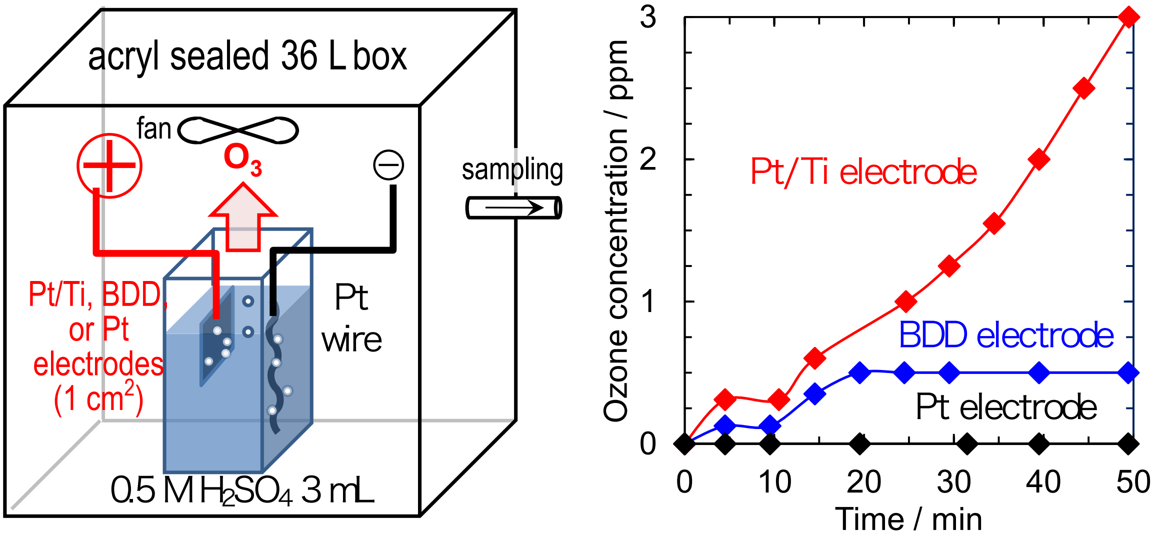

Figure 1. Schematic illustration of the evaluation method (left) and ozone generation activity (right) of the electrodes.

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Influence of Nanoparticle-Electrode Collisions on the Electrodeposition of Pt Nanostructures and their Electrocatalytic Properties

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The deposition of metallic nanostructures via electrochemical methods has received significant attention given the control over composition, size and shape that can be achieved in a relatively facile manner[1-2]. In particular the electrodeposition of Pt has been widely studied given its inherent high catalytic activity for reactions relevant to fuel cells. The ability to change the activity of the surface while at the same time maintaining stability is important for these types of reactions. Many methods have been used to improve activity by generating surface active sites such as electrochemical treatments involving hydrogen evolution, repetitive oxide formation and removal and square wave potential cycling in electrolytes of varying composition. Recently, a relatively new method has been introduced to control the morphology of electrodeposited metals and surface activity namely via a dynamic seeding route utilising nanoparticle collisions with the working electrode during electrodeposition[3].

In this presentation a brief overview of this approach is given for the case of Au and Ag electrodeposition which is then extended to the electrodeposition of Pt nanostructures in the absence and presence of citrate capped Pt nanoparticles (Pt-cit) in the electroplating solution which resulted in the fabrication of Pt with significantly different morphology on a glassy carbon electrode (GCE) (Figure 1).

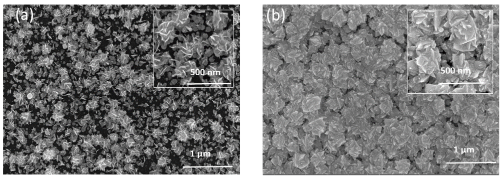

Figure 1: SEM images of Pt electrodeposited in the absence (a) or presence (b) of Pt-cit.

Even though the surface area of the electrodeposited Pt in the absence and presence of Pt nanoparticles was found to be very similar, the electrochemical activity for methanol oxidation was significantly different (Figure 2a). Therefore the use of Pt nanoparticles in solution that collide with the GCE during the electrodeposition process create a continuous source of nucleation sites that not only affects the morphology of the electrodeposited Pt but also its activity. Furthermore the Pt nanostructures created via this approach maintained higher activity with time (Figure 2b).

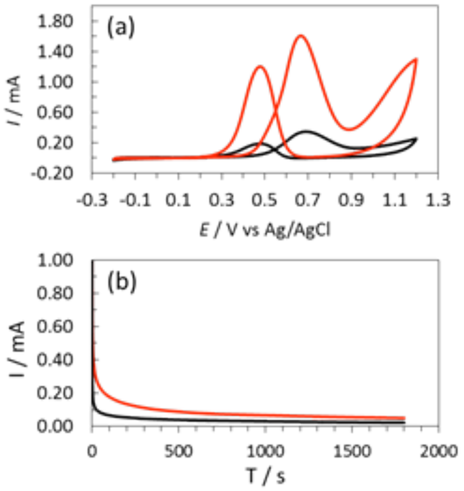

Figure 2: (a) CVs recorded at 20 mVs^{-1} in 1 M methanol in 1 M H_2SO_4 for Pt nanostructures electrodeposited in the absence (black) and presence (red) of Pt-cit, (b) chronoamperometric data recorded at 0.8V for 1800 seconds.

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The Carbon Electrode/Deep Eutectic Solvent Interface – Electrochemistry and Spectroelectrochemisry

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Deep eutectic solvents have been advocated as cheap and environmentally benign alternatives to classical room temperature ionic liquids [1, 2]. For a more widespread use of these types of electrolytes in electrochemical applications a better understanding of their interfacial behavior is required.

In our search for hydrogen-free zinc plating we have studied the electrodeposition of zinc from a deep eutectic 1:2 molar mixture of choline chloride and ethylene glycol containing $ZnCl_2$ and observed unusual voltammetric behaviour at static and rotating glassy carbon disc electrodes [3]. A ligand exchange of the Zn complexes upon cathodic decomposition of the electrolyte occurs before Zn is cathodically deposited during the anodic reverse sweep [4]. This mechanistic hypothesis has been corroborated by the results obtained upon variation of the electrode material, where Zn was deposited from the same electrolyte on graphene, Pt, Au, Cu, Zn, and stainless steel [5]. The electrochemical behaviour of the electrolyte on all of these electrode materials indicates that – apart from the formation of surface alloys – adsorption of the electrolyte components also plays a role in this electrode reaction.

The first *in situ* polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS [6]) studies of a glassy carbon/deep eutectic solvent interface show the extremely slow formation of an adsorbate at open circuit potential [7]. Below –0.4 V vs. Zn/Zn^{2+}, presumably adsorbed hydrogen and/or choline blocks the electrodeposition of zinc. The spectroelectrochemical results indicate a potential-dependent rearrangement of the interfacial architecture.

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The Electrochemical Behaviour of Magnesium Alloys for Secondary Magnesium Ion Batteries

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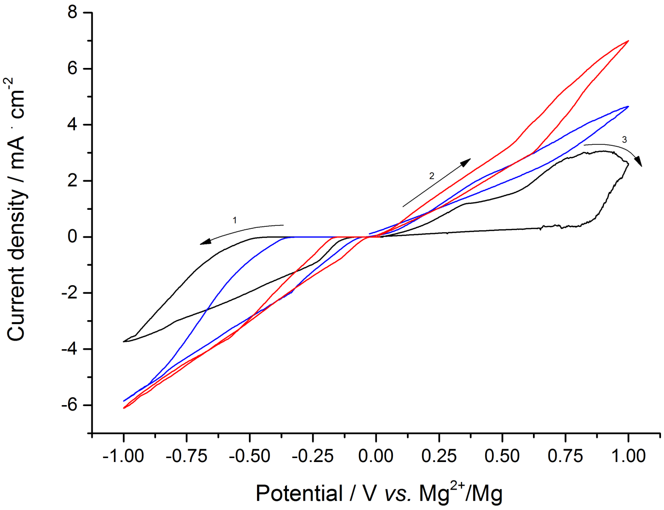
Secondary batteries play a crucial role to fulfill today's increasing demand on portable energy storage systems. Lithium batteries might meet these needs, but they suffer from several drawbacks like dendrite formation, which can even lead to thermal runaway. This behaviour also prevents the use of Li metal anodes. In comparison to lithium, magnesium does not show dendritic electrodeposition and therefore the metal itself could be used as anode material. According to the pioneering work of Aurbach *et al.*, who introduced an electrolyte that is virtually fully reversible and a cathode material, which is stable for many cycles, magnesium is a promising candidate for future battery applications [1-3].

Due to its negative electrochemical reduction potential, magnesium reacts readily with oxygen and water. Unlike aluminium, the oxide layer does not prevent the bulk material from further corrosion. Therefore, it is essential to alloy magnesium to improve its corrosion stability and also its workability. Addition of zinc can improve the corrosion stability, and gadolinium, to improve the ductility and the ultimate tensile strength [4-6].

We report on the electrochemical behaviour of the alloys Mg-1.5 wt.% Zn, Mg-1.5 wt.% Gd, and Mg-1 wt.% Gd-1 wt.% Zn in 0.25 M 2:1 APC-electrolyte [7]. The concentration of the alloying elements and the oxygen content were determined by X-ray diffraction and glow-discharge optical emission spectroscopy. Cyclic voltammetry (Figure 1) and galvanostatic cycling was conducted in a three-electrode arrangement with the respective magnesium alloy as working and auxiliary electrodes.



Error! Reference source not found.: Cyclic voltammograms of MgZn (black), MgGd (blue), and MgGdZn (red) in 0.25 M APC electrolyte, v = 50 µV/s, starting at 0 V in cathodic direction.

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Performance Enhancement of Capacitive Deionization by Using Ionomer-Combined Carbon Electrodes

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Ion selective polymers (ionomers) are currently widely used in water treatment applications such as the diffusion dialysis, electrodialysis, and capacitive deionization for the desalination of brackish water, production of table salt, recovery of valuable metals from the effluents of metal-plating industry, and recoveries of acid and base from the spent leaching solutions. The functional ionomers are also utilized in various energy devices such as polymer electrolyte membrane fuel cells, redox flow batteries and so on. Especially, capacitive deionization (CDI) is thought to be one of the attractive environmentally-friendly desalination processes. It consumes relatively small energy for operation compared with other competing processes such as reverse osmosis. In addition, it does not produce any secondary regeneration wastes for a re-use. Comparing to the conventional CDI, membrane-CDI and ionomer coated-CDI have gained great interests due to the higher ion selectivity and removal efficiency. In this work, therefore, we have synthesized and characterized functional ionomers for the successful CDI application. The anion-exchange polymer was made from poly(2,6-dimethyl-1,4-phenylene oxide) through the bromination and consecutive amination processes. Meanwhile, the cation-exchange polymer was prepared via the sulfonation of polyetheretherketon. In addition, cross-linking agents (e.g. glycidyl methacrylate and polyethylene glycol diacrylate) and specific ion selective resin powder were added into the ionomer solutions to form inter-penetrating polymer networks (IPNs) for better stability and ion selectivity. The functionalized ionomers exhibited excellent electrochemical properties of both the low electrical resistance and high ion selectivity. As a result, the functionalized ionomers which were coated on porous carbon electrodes largely improved the current and salt removal efficiencies of the CDI process.

This work was supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea (NRF-2015H1C1A1034436) and also by the Technology Innovation Program funded by the Ministry of Trade, industry & Energy (MOTIE) (No. 10047796).

Towards Improved Ordering of Self-Organized TiO_2 Nanotube Layers

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The synthesis of highly-ordered nanostructures of valve metal oxides has attracted huge scientific and technological interest due to their possible use in many applications. About 2 decades ago, nanoporous Al_2O_3 had been prepared by the anodic oxidation of Al under suitable electrochemical conditions. A perfectly ordered honeycomb-like porous structure was received (1). Owing to the flexibility of the pore diameter and length and the relative ease of the Al_2O_3 dissolution, its porous membranes have been since than widely used as template material of the choice for a range of materials (2-4).

During the last 10 years, nanoporous TiO_2 has received a similar attention as Al_2O_3 due to its wide range of applications, including photocatalysis, water splitting, solar cells and biomedical uses. Very significant research efforts have led to reproducible synthesis of self-organized TiO_2 nanotube layers by means of anodic oxidation, during which the starting Ti substrate was converted into highly-ordered nanotubular layer by anodization in suitable electrolytes (5-7). However, although advancements were presented during the last years (8) the degree of ordering of the TiO_2 nanotubes produced by anodization did not reach the level known from porous Al_2O_3. Numerous factors influence the ordering and the homogeneity of the TiO_2 nanotube layers.

In this presentation, we demonstrate significant advancements in the ordering of anodic TiO_2 nanotubes compared to known state-of-art. We will show by means of SEM, AFM and optical measurements how to obtain a high degree of ordering, uniformity and homogeneity in the nanotube structure of TiO_2 by tailoring the anodization protocol (9, 10). Furthermore, based on SEM, EBSD and TEM measurements, we will demonstrate how the Ti grain structure influences the lateral uniformity of the nanotube layers (11).

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Electrode Processes and the Performance of the Zinc-Cerium Redox Flow Battery

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Redox flow batteries (RFBs) are an emerging technology addressing the essential requirement of energy storage from sustainable sources. The zinc-cerium hybrid RFB provides an open-circuit cell potential of 2.48 V, the highest for any aqueous RFB. The low toxicity and moderate cost of its electrolytes are also advantageous, in contrast to the potential bromine emissions of the zinc-bromine RFB or the high cost of reagents used in the all-vanadium RFB. During discharge, the zinc-cerium RFB is based on the reduction of Ce(IV) to Ce(III) ions at the positive electrode and the simultaneous oxidation of metallic zinc at the negative electrode. Aqueous methanesulfonic acid is used as supporting electrolyte, enabling a high concentration of cerium ions and facilitating compact zinc electrodeposits. The current state of the art has recently been reviewed [1].

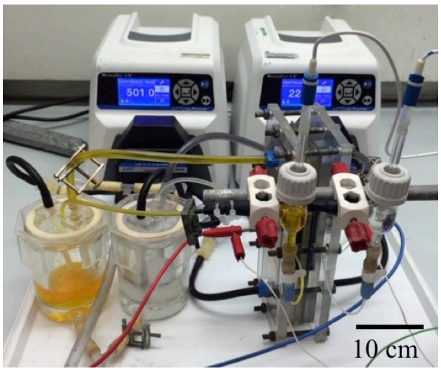

Fig 1. Laboratory zinc-cerium redox flow battery arrangement. Projected area of electrodes 25 cm^2. Operational current < 10 A.

Platinized titanium electrodes show high electrocatalytic activity for cerium oxidation and reduction reactions and their activation overpotentials have been shown to make a significant contribution to cell potential losses [2]. In this work the cell potential *vs*. current density profiles were obtained for various planar and porous (e.g. mesh, foam) Pt-Ti electrodes and related to the reaction environment, showing that high-surface area structures increase battery performance. The experimental arrangement is presented in Fig. 1. The supply of active species and parasitic oxygen evolution reaction govern the relationship between the battery cell potential and the useful current density. These profiles depend on the electrolyte flow rate and the product of the mass transport coefficient and volumetric area, $k_m A_e$. This performance factor is important in cell design and was measured for the evaluated electrodes. The composition of alternative positive electrode materials, mainly cost-effective carbon-based electrodes, is also considered. Presently, the low stability of these materials under Ce(IV) ions is a major limitation of the system. Catalyst modification and coating could improve their activity and stability. Aspects that need critical R&D have been identified. Further research will evaluate zinc deposition at the negative electrodes under mass transport control and in the presence of impurities in the negative electrolyte.

Keywords: cerium, electrocatalysis, electrodeposition, flow, energy storage, mass transport, redox flow battery, zinc.

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Development of Pore-Filled Ionomer Membranes for Efficient Membrane Capacitive Deionization Application

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Capacitive deionization (CDI) is one of the promising desalination processes. It consumes relatively small energy for operation compared with other competing processes such as reverse osmosis. In addition, it does not produce any secondary wastes for a re-use. Comparing to the conventional CDI, membrane-CDI (MCDI) which uses porous carbon electrodes together with ion-exchange membranes (IEMs) has gained great interests due to the higher ion selectivity and removal efficiency. IEMs have been widely used in various water treatment processes for the desalination of brackish water, the production of table salt, the recovery of valuable metals from effluents of metal-plating industry, the recovery of acid and base from spent leaching solutions and so on. Recently, the IEMs have also gained increased industrial importance in the energy conversion and storage processes such as reverse electrodialysis, fuel cells, and redox flow batteries. However, the high membrane cost is considered as one the main obstacles limiting the wide applications of the IEMs. In addition, the properties of the IEMs should be optimized for the specific applications. In this work, we have developed a pore-filled IEMs (PFIEMs) for the applications to cost and energy efficient CDI processes. The PFIEMs composed of a highly inert and tough porous substrate and a polymer with functional groups that fills the pores can provide both high ion conductivity and excellent mechanical properties. In addition, the PFIEMs could be produced in a cheaper way by a roll-to-roll continuous process. The PFIEMs with a film thickness below 50 μm have been successfully prepared and characterized via various electrochemical analyses. As a result, they were shown to possess excellent electrochemical and mechanical properties. Their electrochemical characteristics have also been optimized for the successful applications to MCDI processes.

This work was supported by the Human Resource Training Program for Regional Innovation and Creativity through the Ministry of Education and National Research Foundation of Korea (NRF-2015H1C1A1034436) and also by the Technology Innovation Program funded by the Ministry of Trade, industry & Energy (MOTIE) (No. 10047796).

The Water Impact on Interface Metal Electrode/ Ionic Liquid as Studied by Impedance Analysis

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In alternative energy devices the medium temperature polymer electrolyte membrane (PEM) fuel cells are of growing importance. It resulted in rising interest in field of ionic liquids as components for polymer membranes due to higher temperature range (100-200^{o}C) and electrochemical stability.

In this work the sulfonated polyetheretherketone (SPEEK) polymer was used for composite formation. Ionic liquids (IL) synthesized and examined in this paper included different R-imidazolium dimethyl phosphates [1]. Double cross-linked SPEEK membranes prepared by using chlorosulfonic acid and casted from dimethylformamide solution [2]. An ionic liquid added to the polymer solution.

Complete removal of water from room-temperature ionic liquids is nearly impossible. For the electrochemical applications of ionic liquids, how water is distributed in the electrical double layers when the bulk liquids are not perfectly dry can potentially determine whether key advantages of ionic liquids, such as a wide electrochemical window, can be harnessed in practical systems [3].

Metallic electrodes (Pt, stainless steel) were used for electrochemical characterization of ionic liquids and membranes by impedance analysis. A computer controlled frequency response analyzer FRA with module (Autolab PGSTA–30 for Windows version 4.9) was used in impedance measurements. The impedance spectra were measured in a frequency range from 0.01 Hz to 100 kHz with AC potential amplitude of 10 mV at 20-150 °C. Impedance spectra were measured at different polarization potentials. Water content was determined using Karl-Fischer method. Laboratory made electrochemical cell was used in all electrochemical experiments.

Equivalent circuit method was used to analyze the impedance data. The task was to reveal the water impact on equivalent circuit elements and suitable equivalent circuit for analysis. Also to define the limitations of the method.

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Presentation Method (Poster/ Invited Oral 15/20/25/30minutes): Poster

Direct Writing of 3D Conducting Polymer Arrays for Cell Sensor

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Cell based biosensors which can be used to detect the existence or monitor the behaviour of cells bring great convenience to cell related studies. These lab on a chip devices, can be applied to, for example, sense circulating tumor cells, monitor the movement/proliferation/stimulation-response of cells and even to direct cellular processes such as cell survival, proliferation, differentiation, and migration.

Among various techniques that have been recently explored, nano/micro-structured conducting polymers (CPs) emerged as a promising solution. Compared with traditional materials, CPs have a great many of advantages such as simplicity for nano/micro structure fabrication, intrinsic electrical conductivity, able to be grafted with various functional groups, biocompatible and good mechanical properties. Meanwhile micro/nano structured surface will provide increased cell sensing sensitivity.

Here we put forward the design of direct-written CPs for cancer cell sensors, which may possess improved properties, like high capture rate, selectivity and viability of cells, as well as low time and economic cost during detection. Our research plan is as follows:

1. Direct writing of PEDOT or polypyrrole (PPy) microwire arrays on individual controlled Au electrodes. We plan to prepare CP arrays with different diameters, lengths or different electrochemical properties to figure out the effects of writing parameters.
2. Surface modification with functional groups to improve sensing performance.
3. Characterise the property variation of CP arrays with the presence of living cells, to optimise sensing parameters and analysis efficiency, sensitivity and stability of the overall device.
4. Further development for single cell monitoring or to guide the behaviour of cells by individually applied voltages to different wires.

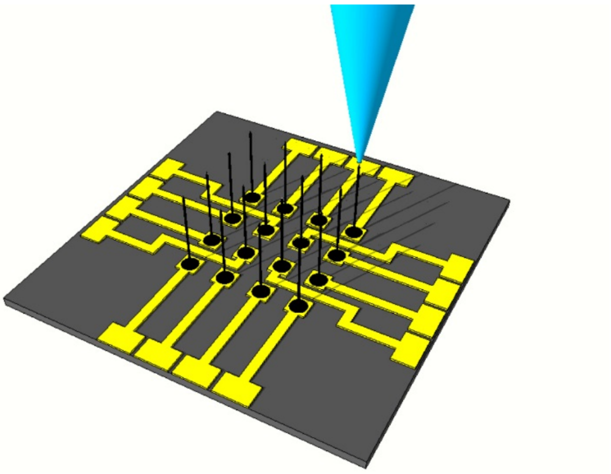

Figure 1. Scheme of 4×4 CP arrays fabricated by a micropipette.

Electrocatalysis of the Hydrogen Evolution Reaction in Acidic Media using Transition Metal Clathrochelates

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Platinum (either in the form of unsupported nano-particles or in the form of nano-particles deposited at the surface of carbonaceous materials of large surface area) is extensively used in Polymer Electrolyte Membrane (PEM) water electrolysis technology as catalyst for the hydrogen evolution reaction (HER). Only two reactions paths involving two steps each are regarded as likely to occur in acidic media (in the followings, H_{ad} denotes a surface ad-atom and M a surface metal site) [1-2]:

Mechanism 1 (Volmer-Tafel)

$$H^+ + 1\ e^- + M \longleftrightarrow MH_{ad} \qquad \textbf{(1-a)}$$
$$2\ MH_{ad} \longleftrightarrow 2\ M + H_2(g) \qquad \textbf{(1-b)}$$

Mechanism 2 (Volmer- Heyrovsky)

$$H^+ + 1\ e^- + M \longleftrightarrow MH_{ad} \qquad \textbf{(1-a)}$$
$$H^+ + 1\ e^- + MH_{ad} \longleftrightarrow M + H_2(g) \qquad \textbf{(1-c)}$$

The first step (Volmer step, 118 $mV.dec^{-1}$) is shared by both mechanisms. They only differ by the desorption step (chemical desorption for mechanism 1 via the Tafel desorption step 1-b that implies surface-diffusion of H_{ad} species at 59 $mV.dec^{-1}$, or electrochemical desorption for mechanism 2 via the Heyrovsky desorption step 1-c at 39 $mV.dec^{-1}$). In the literature, there is a general agreement that on platinum, the HER mechanism is that of a fast proton discharge followed by rate-determining chemical desorption (mechanism 1, step 2 is rds). Whereas the relative cost of platinum group metal (PGM) electrocatalysts in industrial PEM systems is limited to a few percent, there is still a need to anticipate future cost reduction requirements and to develop alternative low-cost electrocatalysts that could sustain significantly high operating current densities (in the multi $Amp.cm^2$ range) and would remain stable on the long-term (for market implementation, operation in the 10^4-10^5 hours range of operation is desirable). Ideally, catalyst containing transition metals (Ni, Co, Fe) should be used. The purpose of this communication is to report on the interest of using a family of transition metal clathrochelates such as the iron compound shown in Fig. 1, adsorbed at the surface of carbon microfibers (Fig. 2) of large surface area, in place of Pt. Chemical structures (powder, in solution and after adsorption) have been determined by XRD and Exafs analysis. Redox properties have been determined by cyclic voltammetry (Fig. 3) and analyzed with the support of DFT calculations. Stationary current – voltage relationships have been recorded. The HER mechanism at the surface of carbon-based working electrodes, surface-modified by adsorption of complexes, has been determined from Tafel plots and by using electrochemical impedance spectroscopy. These complexes have also been implemented at the cathode of PEM water electrolysis cells. Electrochemical performances have been measured at different temperatures, over an extended range of current density. Stability has been demonstrated over 1,000 hrs of continuous operation.

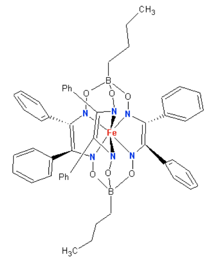

***Fig. 1 :** Structure of iron clathrochelate.*

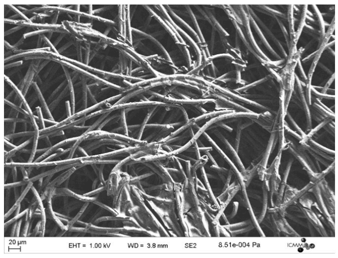

***Fig. 2 :** SEM micrograph of carbon micro-fibers.*

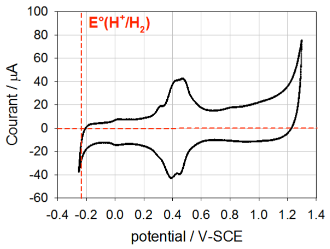

***Fig. 3** : Cyclic voltamogram measured at 25°C in H_2SO_4 0.5 M.*

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The use of a bi-metallic structure under cathodic protection in seawater favors a 3D calcareous growth imitating the coral structure

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One of the consequences of the cathodic protection of marine structure in seawater, by galvanic coupling with a sacrificial anode or by application of a fixed current density with an inert anode, is the precipitation of calcareous deposit on the metal surface. The principle of the deposition is well known. It consist of the reduction of dissolved oxygen and water, depending on the applied potential or current, that increases the interfacial pH and thus the precipitation of brucite $Mg(OH)_2$ and aragonite $CaCO_3$ that compose the calcareous deposit. When applied on a metallic surface, the deposit tends to cover the whole surface uniformly and is benefit to reduce the electric consumption. In the case of a bi-metallic structure, the potential of water reduction could be different giving rise to inhomogeneous deposit. For example, the over-potential of water is about -200mV compare to carbon steel.

In our experiments, we study the formation of the calcareous deposit first on commercial galvanized steel wires by potentiostatic polarization at different temperature. The main goal is to follow the influence of the Zn layer on the kinetics of deposition and how the partial dissolution of this layer, in the case of low cathodic potential, change the nature of the deposit due to the reactivity of the water on steel.

Then, a bi-metallic wire was used in a galvanic polarization mode in order to control the reactions both on steel and on the zinc layer. Two environments are used: artificial seawater that complies with the ASTM norm D1141 (American Society for Testing Materials) and filtered/purified natural sea water. A large water volume (2 L) is used, avoiding depletion of cations during the formation of deposits. The temperature is fixed using a controlled heating resistance, from 25 to 50°C.

The calcareous deposit has been analysed by Scanning Electron Microscopy (SEM), µ-Raman spectroscopy (surface and cross section) and by X-Ray diffraction. Our results on galvanized steel wires show that the corrosion potential is not affected by the temperature, and potentiostatic experiments exhibits an increase of the current density due to the reduction of the Zn coating layer for low cathodic potentials. For higher cathodic potential, voltammetry experiments induce a voluminous deposit that can grow with time. The final composition and element distribution (brucite vs. aragonite) vary with temperature. For bi-metallic structure, the current passed for the most part across the steel giving rise to a thick brucite deposit whereas on the zinc layer, a very thin hydrogen bubble formation due to a lower current gives rise to the formation of a 3D calcareous structure that mimics the formation of natural coral.

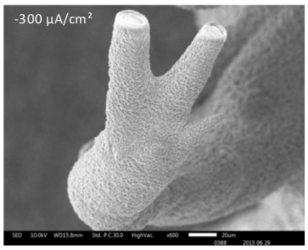

figure : SEM image of a coral-like shaped calcareous deposit.

This work is co-funded by the "Fonds Pacific" (French Foreign Office) and French Research National Agency (ANR) and is a part of the project "EcoCorail".

Electroactive Electrospun Semi-Interpenetrated Network Fibre Mats with Controllable Pore Sizes

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In this work we describe the synthesis of new electroactive microfiber mats using the electrospinning technique. Microfibers have been in-situ prepared from a solution of Nitrile Butadiene Rubber (NBR) and crosslinked in the presence of polyethyleneglycol dimethacrylate by UV-irradiation during electrospinning.

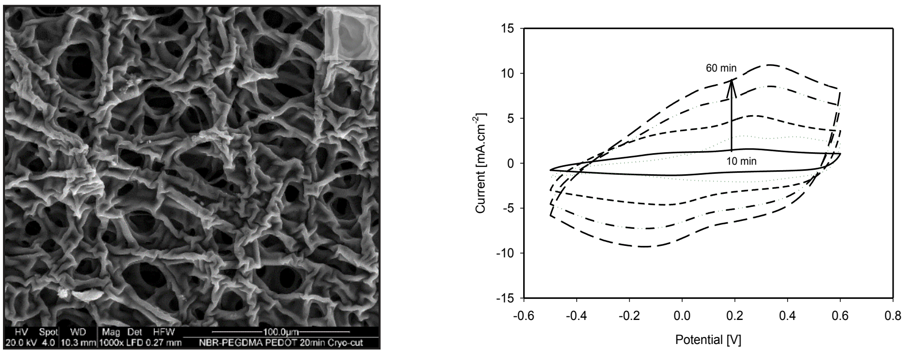

Figure 1. Electrospun NBR/PEGDM elastomeric fibres (a); and cyclic voltammogram of the fiber mat in 1 M LiTFSI propylene carbonate solution (b).

These electrospun mats have then been swollen with (3,4-ethylenedioxythiophene) (EDOT) followed by polymerization in 1.5 M $FeCl_3$ aqueous solution leading to conducting NBR/PEDOT SIPN based nanofibrous materials. These mats show high flexibility, an electrical conductance as high as 10 $S.cm^{-1}$ and high electroactivity as shown by cyclic voltammetry (Figure 1b).

The mats were then actuated electrochemically and the change in the average pore size was measured. When swollen in 1 M LiTFSI PC solution the average pore size increased reversibly by 25 % upon reduction.

To enhance the mats performance in aqueous media, poly acrylic acid (PAA) was grafted off the surface of the fibres via ATRP. This results in hydrophilic fibres whose electrochemistry can be stitched through altering the pH (Figure 2).

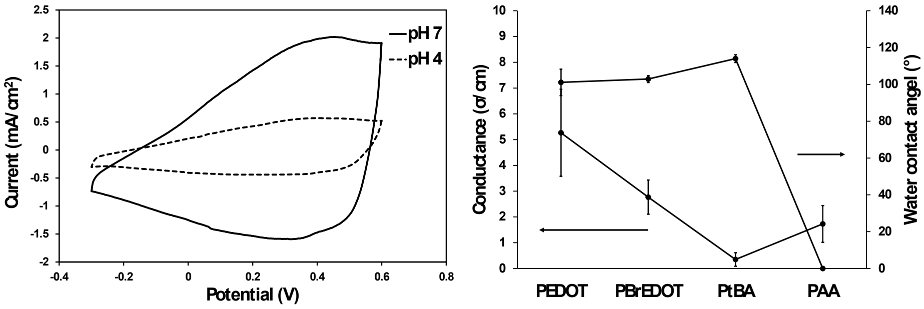

Figure 2 Cyclic voltammogram of PAA grafted PEDOT embedded fibres in 100 mM NaCl aqueous solution with a citrate buffer at pH 4 and 7 (left) and conductivity (S/cm) and water contact angle at different stages of fibre grafting.

The influence of Rh in Pt-Sn/C nanocatalyst for ethanol oxidation: Physical and electrochemical characterization

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Carbon supported bimetallic Pt-Sn and trimetallic Pt-Sn-Rh nanocatalysts were synthesized by Bönnemann's colloidal precursor co-reduction method [1, 2]. Electrochemical characterization of the catalysts regarding their onset potentials, activities and current densities towards ethanol oxidation were determined by linear sweep voltammetry [2]. The relationship between the catalyst structure and catalyst activity of was evaluated by various microscopic and spectroscopic characterization techniques such as X-ray diffraction (XRD), High resolution transmission electron microscopy (HR-TEM), Energy dispersive X-ray analysis (EDX), and in-situ Fourier transform infrared spectroscopy (FTIR) [2-4]. It was found that the catalytic property of Pt-Sn/C for the ethanol oxidation is favorably altered in the presence of Rh. To understand the benefits of Rh in the structure of Pt-Sn/C, HR-TEM and EDX spectroscopy techniques was very helpful since the particles with different phases such as SnO_2 species can be clearly observed from high resolution images. The analysis result showed that SnO_2 and Pt-Rh exist as separate state in the Pt-Sn-Rh/C catalyst (Fig. 1). The change in the Pt lattice due to the addition of Rh and to interaction between Pt and Rh, both of which favors C–C bond cleavage in the ethanol molecule, while the CO-intermediates formed during breaking of C–C bond were removed by the SnO_2 surface species.

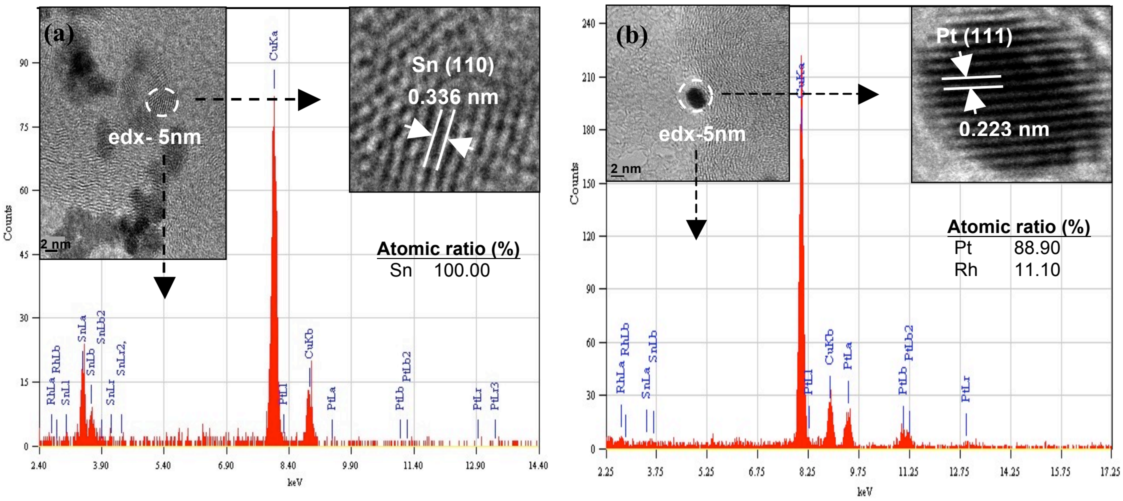

Figure 1. HRTEM images of Pt-Sn-Rh/C catalyst together with EDX analysis of the selected areas, showing the particle has the SnO_2 structure (a) and Pt structure (b) using a 5 nm electron beam.

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Grafted Conductive Polymer Surfaces for Switchable Electrochemistry and Modulation of Cell Adhesion

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Our work on conductive polymer (CP) systems grafted with stimuli responsive polymer brushes is motivated by the prospect of creating surfaces with electrically switchable properties, such as contact angle or protein and cell binding. We have synthesized a range of novel CP monomers bearing sites for grafting of polymer brushes by controlled radical polymerization. By tailoring the grafted brushes (type, composition, length and grafting density) materials with switchable surface properties are produced. The commercially important polymer PEDOT was modified with an ATRP (atom transfer radical polymerization) site and used to graft pH responsive poly(acrylic acid) brushes from. Characterization by Cyclic Voltammetry and Surface Plasmon Resonance revealed that pH driven conformational changes modulates the electrochemistry of the films and also indicated electrically induced conformational changes.[1]

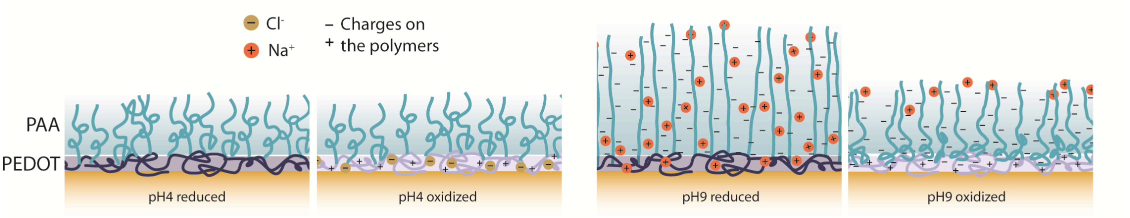

Figure: Proposed response of PEDOT-g-PAA to changes in pH and electrical potential.

A platform for investigating cell adhesion to grafted conductive polymer materials was developed. Firstly, the effects on cell adhesion by applying a potential to PEDOT during both protein coating and during cell culture was investigated. The results highlight the importance of pre-adsorbing fibronectin in this case, especially for the reduced polymer which binds protein strongly. The effects of changing the surface chemistry of the PEDOT electrode by grafting of brushes by atom transfer radical polymerization was also investigated. Specifically, the composition of the salt-sensitive poly(oligo(ethylene glycol methyl ether methacrylate))-based brushes was tailored to control the level of cell adhesion to the interface.[2] The composition, but also the length of the grafted brushes was seen to be important to the cell adhesion. It was also demonstrated how PEDOT films grafted with a protein and cell rejecting brush could be converted to a cell adhesive state by attaching an integrin ligand to the brush to mediate cell adhesion.[3]

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Effect of Alumina and Titania Barrier Layer on Zinc Electrodeposition from Deep Eutectic Solvent

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The use of high-ordered porous templates formed on valve metals to obtain nanostructures via electrochemical deposition is a cheap and convenient method. However direct investigation of deposition and nucleation processes on the barrier layer of the porous templates is difficult because the interface is hidden. Moreover diffusion limitations in the pores can create additional complications. On the other side deep understanding of the processes, which occur in the beginning of the deposition, is extremely important because they influence markedly the properties and structure of the deposited materials. Electrodeposition on flat samples allows avoiding restrictions from porous templates and are used as a suitable model process.

In this work, zinc electrodeposition from a solution of $ZnCl_2$ in a choline chloride / ethylene glycol eutectic mixture (DES:Zn) on dense alumina and titania layers was studied. The effects of the oxide layer thickness and applied potential profile on deposition were investigated.

In DC potentiostatic regime, the deposition on an alumina barrier layer was found to be hardly possible even when this layer is a native alumina film (about 2 nm thick). Choline and ethylene glycol form an adsorbed stable layer at the alumina/electrolyte interface, which blocks the access of zinc chloride anions to the electrode. However zinc can be directly deposited on a barrier layer at ambient temperature by means of application of a combined potentiostatic mode, consisting of an AC component superimposed on DC potential of -1.6 V. Increasing the temperature of the eutectic solution allows zinc electrodeposition in the only d.c. potentiostatic regime. The range of frequencies of the AC component and the temperature range where the deposition is optimal were considered. The mechanism of unblocking of the electrode by the alternating potential and by the temperature rise has been suggested.

Titanium/titania and aluminium/alumina systems despite chemical similarity demonstrated different properties. Whereas in the case of the alumina barrier layer the current decreases with increase of its thickness [1], in the case of titania the behavior is different. Voltammograms that were obtained on the titanium electrode covered by compact titania film in DES:Zn showed that the negative current on a 18 nm thick titania film is similar to the one for a 12 nm film and further increment of thickness to 23 nm and higher causes the increase of current. The maximum current was obtained at a film thickness of 84 nm and is similar to the current on the activated electrode. This could be explained by progressive increase of film crystallinity and conductivity with growth as has been suggested in the case of copper deposition [2].

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Solvent vapour-induced healing of conducting polymer blends

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Abstract

Recent advances in organic electronic devices have reached a new milestone in performance and function in various areas. These applications vary from displays to sensory devices. However they still present limitations in mechanical flexibility and electrical durability following the damages caused during their lifetime. Herein, we present a facile preparation and solvent vapour-induced healing of conducting polymer blend films that can address such limitations mentioned above. They have been prepared by simple solution blending of doped poly(3-hexylthiophene) (P3HT) and poly(dimethylsiloxane) (PDMS)-containing urea segmented copolymer solutions. The resulting film with 30 % weight fraction of P3HT was directly casted and its electrical, electrochemical and mechanical properties were characterised. Superficial scratch on the surface of the film was made to create a crack both on the surface and within the film. The film showed remarkable electroactivity as well as solvent vapour-induced mechanical healing leading to restoration of the electrical properties.

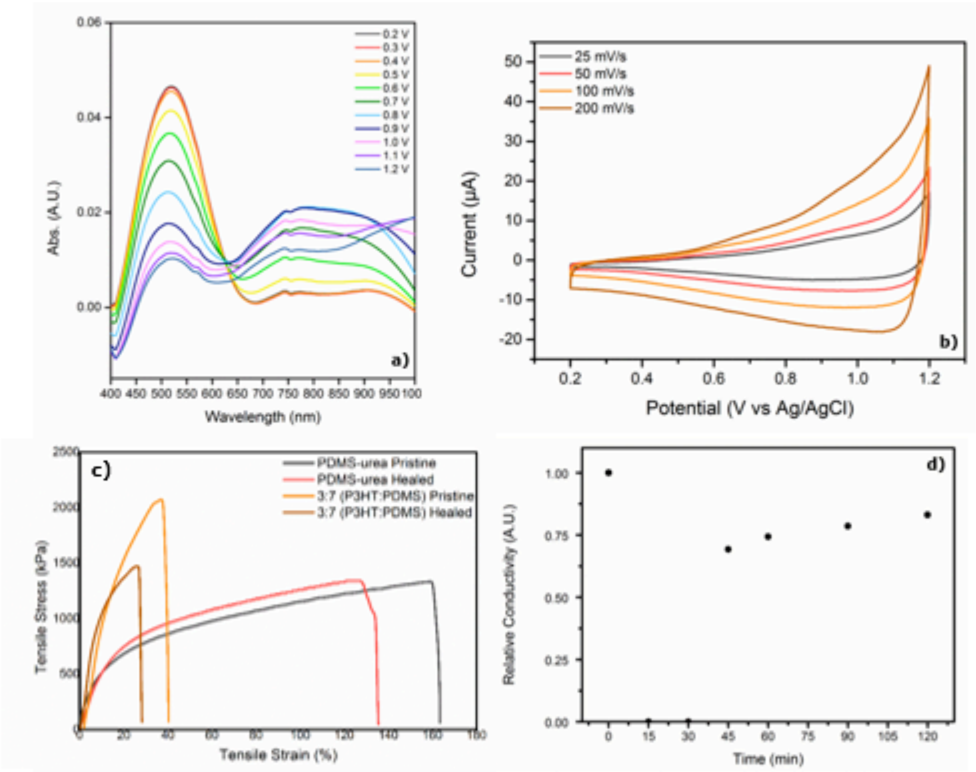

Figure. a) Spectroelectrochemistry and b) cyclic voltammetry at various scan rates of spin coated 30 wt% P3HT blend (3:7 blend) on ITO in 0.1 M TBAHFP in MeCN. c) Tensile strain measurements of samples before and after solvent-induced healing. d) Relative electrical conductivity of 3:7 blend before and after solvent-induced healing at different time intervals.

Electrochemical Deposition on Dielectric-Layered Electrode

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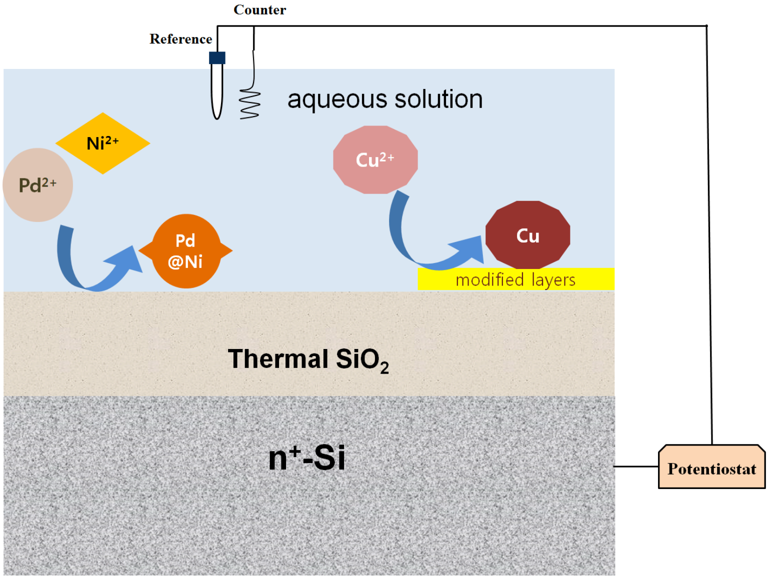
Direct electrochemical deposition on the dielectric supports has a limitation in terms of the types of deposited metals and their dispersity. It was reported that Pd nanoparticles (NPs) were deposited on SiO_2 dielectric layers, which were prepared thermally oxidized on highly n-doped silicon (n^+-Si) electrode by electrochemically generated hydrogen (H) atoms[1]. The migrated protons into thermal SiO_2 layers are reduced into H atoms, which diffuse to the interface between SiO_2 and solution. Then, metal precursors happen to be reduced into NPs. Especially, few-nm thick dielectrics are likely to be functioned as a fine controller of electron transfer for producing NPs. However, there is difficulty in obtaining uniform thin metal films on dielectrics through which current density is too low. Besides, it is hard to deposit other types of metals except Pd due to poor affinity of reduced metal species onto pristine SiO_2.

Here we suggest a new breakthrough for electrochemical deposition of Ni, Cu, Pt, Au, etc. on n^+-Si/thermal SiO_2. In order to increase affinity between reduced metal species and surface of SiO_2 dielectric layers, the modification of SiO_2 surface is conducted. Or, Pd precursors are mixed with other metal precursors in electro-deposition on n^+-Si/thermal SiO_2. The obtained films are composed of nanoparticles, which can be applied as catalysts. Here, Pd-based metal films are successively tested as a hydrogen sensor. Therefore, it is expected that this results may impact on the simple and economic fabrication of metal-insulator-semiconductor (MIS) systems and its application.



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In situ Synchrotron X-ray Studies of Interfaces Under Electrochemical Control

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Synchrotron facilities offer the possibility of conducting *in situ*, real-time experiments to follow electrochemical processes at interfaces. The results obtained allow detailed information to be obtained about chemical speciation, crystallographic phase and orientation, rate kinetics, phase transformations etc. This can then be related to the electrochemical response to provide a deeper understanding of the underlying reactions. In this presentation the benefits of using synchrotron techniques to study electrochemical processes will be shown, briefly demonstrated by a number of examples, as follows:

Redox behaviour of surface oxide films on copper nanoparticles. Quantitative information about the distribution of valence states of copper during the electrochemical reduction of air-formed oxide films on supported copper nanoparticles was obtained using *in situ* X-ray absorption spectroscopy. The initial film consisted of both Cu(II) and Cu(I) oxide species, and the reduction of Cu(II) to Cu(0) proceeded through a Cu(I) intermediate. Interesting overpotential effects were observed in cyclic voltammetry experiments.

Electrochemical deposition of zinc oxide nanorods. Zinc oxide nanorods were fabricated via electrochemical deposition under potentiostatic conditions, and their growth followed using *in situ* X-ray fluorescence. This enabled kinetic information to be obtained with a time resolution of 1 s. In different potential regimes, different growth mechanisms were observed [1]. *In situ* X-ray diffraction studies were performed to determine the development of preferred orientation of the initial nuclei. Despite no morphological indications, the nuclei were found to have a high degree of preferred orientation from the earliest times measurable [2].

In situ corrosion studies of steel in carbon dioxide-saturated environments. The corrosion of steel in aqueous saturated CO_2 environments is a major industrial problem. Under certain conditions a highly protective scale of siderite ($FeCO_3$) is formed; however, there is little information available regarding the initial nucleation processes. *In situ* synchrotron X-ray diffraction studies using electrochemistry to accelerate the corrosion rate have shown the effect of temperature [3], corrosion inhibitor species and concentrations [4-5], addition of Mg^{2+} [6] and Cr^{3+} [7], and steel microstructure [8] on the growth rates of crystalline $FeCO_3$ films. A new method of analysing the development of 'spotty' diffraction rings provides insight into electrochemical roughening of the steel surface that precedes formation of the crystalline film [8-9].

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Modifying Graphene via the Diels-Alder Reaction of an Anthranilic Acid: New Chemistry for Graphene Energy Storage Materials

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The development of a sustainable future for energy is of paramount importance. This includes developing both renewable energy sources and energy storage devices. The outstanding electronic, mechanical, and thermal properties of graphene, along with its extraordinarily large surface area mean it has significant potential as a supercapacitor material. In order to construct workable capacitance devices from graphene it is first necessary to covalently functionalize graphene sheets. This will both improve ease of handling,[1] and provide an opportunity to increase the capacitance of the sheets by introducing defects.[2]

This work explores a novel method for the divalent functionalisation of few-layer graphene. The reaction involves a Diels-Alder cycloaddition of an aryne, generated from an anthranilic acid precursor, to the few-layer graphene sheet. This method is expected to preferentially modify the basal plane of graphene. The films have been characterized by infrared and Raman spectroscopy, atomic force microscopy, and electrochemistry. The electrochemical results indicate that altering either the reaction time or the concentration of anthranilic acid in the reaction mixture can effectively control the surface concentration. Electrochemical impedance spectroscopy and cyclic voltammetry have been used to measure both the differential and integral capacitance of these systems.

This work outlines a novel protocol for the controllable and preferential modification of the basal plane of few-layer graphene sheets. It also begins to explore the energy storage capacity of such systems.

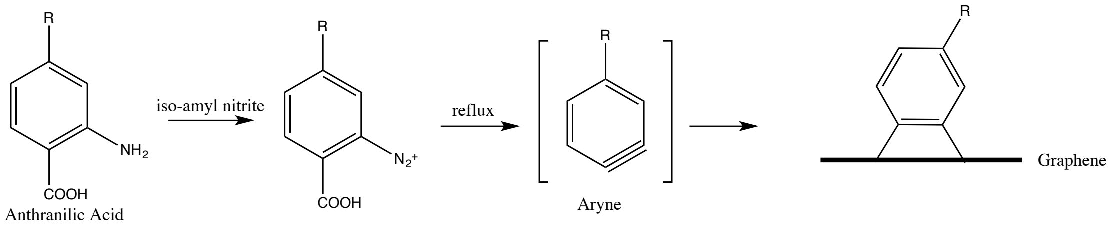

Figure 1: Generation of an aryne, followed by divalent functionalisation of few-layer graphene

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Electrodeposition of zinc 1-D nanoparticles in porous anodic alumina and titania template from deep eutectic solvent.

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The development of one-dimensional nanostructures is currently under active investigation for different applications. Electrochemical preparation of 1-D nanoparticles is a conventional and cheap method. Porous anodic templates on the valve metals are the most common material for that aim. Filling of the templates by a secondary material makes it possible to apply these systems for solid state solar cells, photodetectors, magnetic sensors, metal–insulator–metal capacitor etc.

In the presented work the deposition of zinc nanoparticles inside pores of titania based templates from choline chloride eutectic solution containing $ZnCl_2$ was performed. Often choline eutectic is named in literature as quasi ionic liquid because all properties are similar to them, but in contrast to conventional ionic liquids choline based electrolyte is very cheap, not-toxic and has potential for use in industry. Zinc was chosen as a model metal for deposition due to possibility of subsequent transformation into semiconductor materials such as zinc oxide and zinc sulphide.

Electrodepostion of zinc in titania porous oxide was performed in one step with a pulse technique. Parameters of the pulse were tuned to obtain better fill-factor. The first negative pulse 0.01s is used for reduction of the metal. Than positive current flows through the system during 0.002s for dissolution of zinc from the surface. Relaxation time is 0.988s, and it is necessary for diffusion zinc ions from the bulk solution inside the pores (fig. 2). Different current densities were tested.

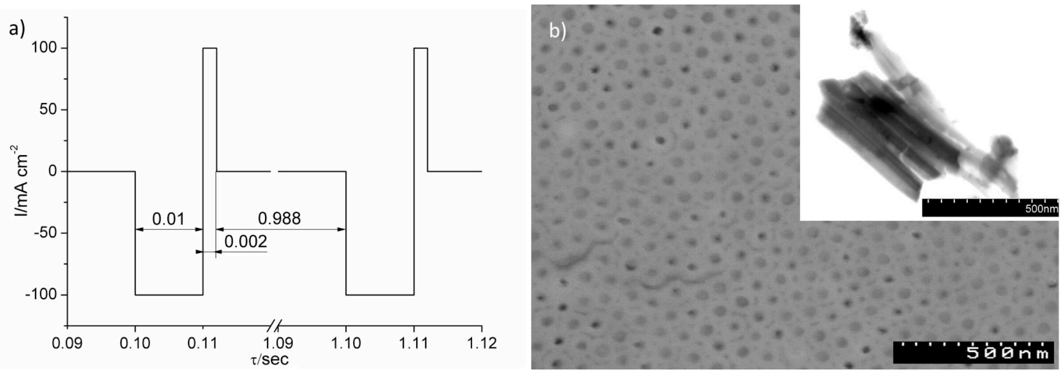

Figure 1. a) Typical shapes of current pulses applied during the deposition process; b) SEM micrographs of the porous titania template filled with zinc; the inset shows STEM image of the sample after deposition;

The influence of the template pre-treatment was also studied. Three main templates types were used. The first is standard template without any treatment. It was dried in the desiccator and was used for deposition. The second template was annealed after preparation at 450°C during 5 hours. This step converts amorphous titania to crystalline and increases conductivity of the oxide. The third type of the pre-treatment is increasing of the barrier layer thickness. Growing of the barrier was performed in 1M H_2SO_4 solution with current density 10mA/cm^2. The process was terminated after the 80 V was achieved. This procedure increases thickness of the bottom oxide and at the same time increases crystallinity and conductivity of the bottom. All these manipulations have strong impact on the electrical properties of the matrix which is demonstrated in the work. Advantages and disadvantages of these templates are presented.

The presence of zinc in the porous system was confirmed by SEM/STEM/EDS and XRD. Additionally, for control filling of the pores glow discharge optical emission spectroscopy was used.

The silver nanoparticles/TiO$_2$ interface: a combined electrochemical and theoretical investigation

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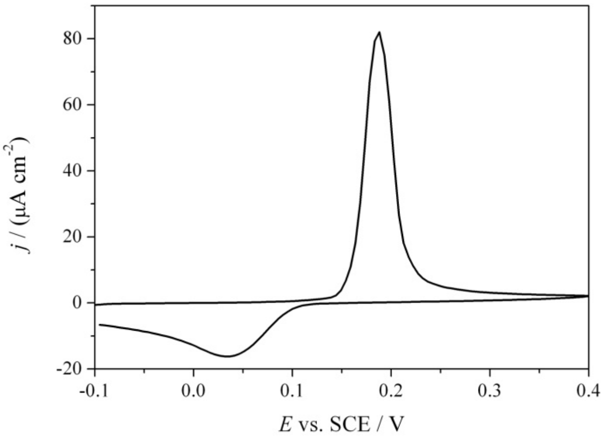
A modified electrode, made by silver nanoparticles covered with a thin layer of titanium dioxide (anatase polymorph) was prepared and electrochemically characterized by cyclic voltammetry and electrochemical impedance spectroscopy. Previously synthesized silver nanoparticles (mean diameter 10 ± 2 nm) were immobilized on an inert support (aminosiloxane-functionalized fluorine-doped tin oxide) and subsequently covered with a 100 nm-thick layer of titania using our previously reported methodology [1].

Electrochemical studies showed a pronounced electrocatalytic effect and an increase in the current intensity of the silver oxidation peak in comparison with the results reported in the literature for uncovered silver nanoparticles [2-4]. Moreover, the resulting composite showed a strong UV light response: complete restoration of the silver oxidation current peak was observed when the composite was irradiated after performing a voltammetric scan, thanks to the UV-assisted reduction of the passivating oxide layer.



These results are explained by theoretical DFT calculations, performed using the VASP code [5-10]. Namely, an interface of silver on the (101) cut of anatase TiO$_2$ was grown and characterized. A commensurate Ag structure was found, showing an interaction in the region of the junction between silver atoms and TiO$_2$. The interaction was justified by the Ag-O distances and the atomic charges computed using a special code [11-13], which takes in input the outputs of VASP. The silver atoms close to the semiconductor gain a partially positive charge, while the oxygens of TiO$_2$ host the negative ones. The charge transfer decreases with the distance from TiO$_2$ and characterizes the metal-semiconductor junction. This theoretical picture allowed us to find a very good agreement between theory and experiment, shining light on a system of both great theoretical and applicative interest.

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Effects of Surface Pretreatment of Glassy Carbon on the Electrochemical Behaviours towards V(IV)/V(V) reaction

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The all-vanadium redox flow battery (VRFB) exploits the redox reactions of vanadium ions in four different oxidation states to realize the conversion between chemical and electrical energy[1]. Due to the unique single-element design, it eliminates the problems of cross-contamination, which makes it outperform other RFBs and achieves extensive commercialization around the world. Although this technology has been developed for more than three decades, the reaction kinetics of VRFBs is still not thoroughly understood. Discrepancies can be easily found in the published studies of V(IV)/V(V) and V(II)/V(III) reactions by various groups[2-15], not only in the magnitude of the calculated rate constants but also in the determination of faster half-cell reaction. Apart from the variation in the experimental conditions, including electrode materials[2,3,11,14], electrolyte species and concentrations[5], pH values[2,5] and temperature[12] during the measurement, differences in the surface status caused by various pretreatment[15] can also lead to widely divergent electrochemical response towards the vanadium redox couples. However, most studies failed to indicate all the factors especially the pretreatment conditions of the electrodes. Therefore, this paper aims to build a systematic way to study the reaction of V(IV)/V(V) redox couples and mainly focuses on the effect of surface roughness and functional groups derived from the pretreatment on the electrochemical behaviour of glassy carbon in V(IV)/V(V) solutions. 600-grit, 1200-grit and 4000-grit SiC sandpaper were utilized to change the roughness of the electrode surfaces. Cyclic voltammetry (CV) within different potential ranges were applied in advance to alter oxygen functional groups as well as the roughness on the electrode surfaces. CV and electrochemical impedance spectroscopy (EIS) were then used to investigate the electrode behaviour in 1M V(IV)/V(V) (1:1) and 2.5M SO_4^{2-} solution on glassy carbon electrodes. Scanning electron microscope (SEM) was employed to characterize the surface roughness. X-ray photoelectron spectroscopy (XPS) was adopted to analyse the surface oxygen functional groups. It is shown that polishing and CV scans within different potential ranges can vary the electrochemical response of glassy carbon to V(IV)/V(V) couples significantly. Rough electrode surface is beneficial for the redox reaction and oxygen functional groups such as C=O tends to reduce the activity of glassy carbon.

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Light Activated Electrochemistry: A strategy for performing voltammetry on a monolithic surface where you want, when you want with micron scale spatial resolution

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Light and electrodes have a long history with spectroelectrochemistry, electrochemiluminescence and photovoltaics. Here we exploit light shined on an electrode to locally activate the electrode surface to allow Faradaic electrochemistry to occur on the illuminated spot only. To achieve this, first an oxide free silicon electrode is modified with a self-assembled monolayer of 1,8-nonadiyne which protects the surface against oxidation. Subsequently a redox species is attached to the surface, either a ferrocene derivative for n-type silicon or an anthraquinone derivative for p-type silicon. Provided the silicon is in the depletion at the potential at which the oxidation/reduction of the redox species occurs, then no electrochemistry is observed in the dark. Upon illumination distinct Faradaic electrochemistry is observed. We show this electrochemistry can be confined to 50 μm with backside illumination and 30 μm with frontside illumination. Subsequently, using SECM we show that the surface bound redox species can be used as a mediator to detect redox species in solution. We next show that we can detect DNA hybridization and form DNA electrode arrays (an example of reading electrochemical information from the electrode surface) and show that we can write conducting polymers to the surface. Finally we demonstrate an application for the capture and localized release of cells from the surface.

Fate of a monomeric Pt^{III} species produced via electrochemical oxidation of anticancer compound *trans*-$[Pt^{II}\{(p\text{-}BrC_6F_4)NCH_2CH_2NEt_2\}Cl(py)]$

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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*-$[Pt^{II}\{(p\text{-}BrC_6F_4)NCH_2CH_2NEt_2\}Cl(py)]$ 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} organoenamineamides) formed by chemical oxidation of the platinum anticancer compound and by exhaustive bulk electrolysis. Relationships between Pt^{III} intermediates and Pt^{II} organoenamineamides 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} organoenamineamide (A) generated by chemical oxidation gives more stable monomeric Pt^{III} on its electrochemical oxidation and it is stable at longer time scales.

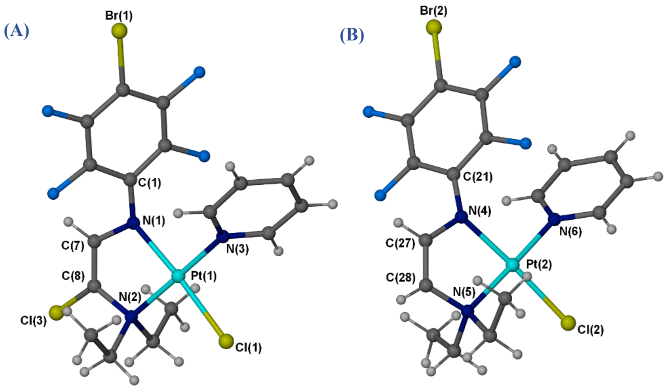

Figure 1. X-ray crystal structures of substituted (A) and non-substituted (B) organoenamineamides obtained after chemical oxidation of trans-$[Pt^{II}\{(p\text{-}BrC_6F_4)NCH_2CH_2NEt_2\}Cl(py)]$ *with hydrogen peroxide.*

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Self Terminated Oligomer Branched Architecture (STOBA) in lithium ion battery

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Lithium ion battery provides high energy and power density that uses into portable electronics and electric vehicle; however, the safety is a big issue and cannot be guaranteed due to different habits of users. In order to improve the safety performance of battery, a new technology called Self Terminated Oligomer Branched Architecture (STOBA) had been developed [1]. The STOBA is used to prevent the direct contact between anode and cathode when the battery suffers short problem. According to the literature [1], STOBA is an oligomer that homogeneously disperses into cathode slurry and electrochemically forms solid electrolyte interface (SEI) on cathode's surface. This SEI provides further isolated polymerization behavior in order to inhibit the decomposition of cathode material while battery gets short.

In this study, second generation of STOBA has been created. Figure 1 shows that the second generation of STOBA is polymerized by BMI/BTA oligomer (1st generation STOBA) and poly(phenylsiloxane) (PhSLX). The PhSLX is used to enhance the thermal and electrochemical stability of STOBA. In accordance with the results, this 2nd generation STOBA not only maintains high safety performance, but the cycle-ability at high temperature also increases.

The second generation of STOBA is a highly potential additive for application in electric vehicle.

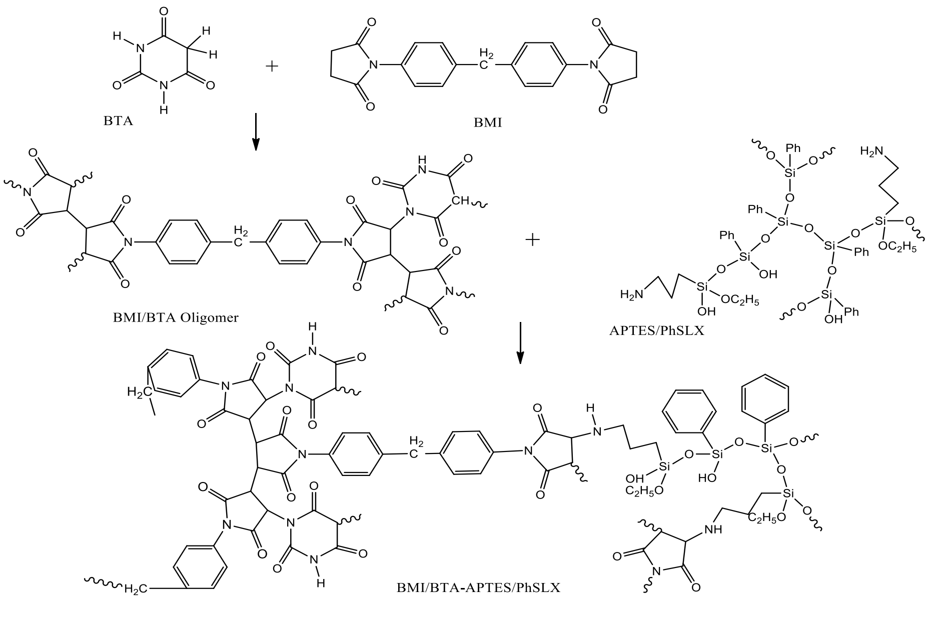

Figure 1 The reaction mechanism of the self-polymerized branched oligomer additive.

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Unzipped carbon nanotubes via KOH activation for high specific surface area and trimodal pore structure

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Abstract

We prepared unzipped CNTs with high specific surface area (1123 m^2 g^{-1}) and a trimodal (micro-meso-macro) pore structure through alkali activation. After severe alkali activation (in our study, CNT (C)/KOH = 1:10 (w/w) at 1000 °C), various pores were initially formed on the surface. Subsequently, a longitudinally unzipped structure was obtained as the individual pores connected. In contrast with other methods to prepare unzipped and porous CNTs, this method is economical and scalable because it enables a one-step synthesis of unzipped and porous CNTs. As per the non-localized density functional theory (NL-DFT), the distribution of micro-meso pores showed evidence of unzipping because the peak for pore sizes <1 nm, measured from the partially opened tips of the pristine CNTs, was broadened. Since the tips were perfectly opened after activation, this means that the micropores on the unzipped structure increased. In addition, the results showed that the unzipped porous CNTs had a trimodal pore structure. This structure resulted in increased specific surface area, as well as energy storage and adsorption capacities. The maximum energy density of the unzipped porous CNTs in ultracapacitors based on an organic electrolyte was 50 W h kg^{-1}. Thus, the method is suitable for fabrication of unzipped porous CNTs, which show potential as energy efficient materials.

Introducing Android Voltammetry

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The rapid expansion of mobile phones and other mobile technologies is set to transform biosensing landscape. In particular the widespread availability of smartphone technology and the capabilities they offer in terms of computation, communication, networking, and imaging will allow a more extensive deployment of lab-on-a-chip and related sensing technologies. Furthermore the combination of mobile technologies with low-cost sensing concepts such as paper microfluidics could make life-changing health and environmental testing technologies available to many millions more people both in the developed and developing worlds. Voltammetry is the cornerstone technique of electrochemical sensing, and almost all dynamic electrochemical methods can be regarded as variations of the basic voltammetric method. We will show for the first time that quantitative voltammetric analysis may be carried out using only the intrinsic hardware in a mobile device such as a phone or tablet, and a suitable software application, using no external device or instrument whatsoever. We call this new approach Android voltammetry.

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) ($[\mathrm{Ru(bpy)_3}]^{2+}$) 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 $[\mathrm{Ru(bpy)_3}]^{2+}$, greatly simplifies the analytical procedure.

Solid electrolyte interphase generation via surface-bonded vinylene carbonate on graphite negative electrode for lithium-ion batteries

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At present, graphite is the most widely used negative electrode for lithium-ion batteries (LIBs). The working potential of graphite is very close (0.2~0.3 V *vs.* Li/Li^+) to the lithium metal, and the commonly used electrolytes are not electrochemically stable under such a highly reducing condition. Resultantly, the electrolytes decompose and the decomposed products deposit on the graphite surface. The surface film, often called solid electrolyte interphase (SEI), then passivates the graphite electrode to prevent additional electrolyte decomposition. In order for the surface film to play its own roles, it should be thin, compact, uniformly covered and thermally stable. The surface films generated from the commonly used electrolytes do not meet the above requirements. Hence, SEI former is frequently added into the electrolyte solution, which decomposes prior to the electrolytes and forms stable SEI layers.

Vinylene carbonate (VC) is widely used SEI former for graphite negative electrode.[1] The critical problem associated with VC is the instability against electrochemical oxidation. Namely, when the high-voltage positive electrode such as $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) is used in LIBs, VC is decomposed to bring serious negative impacts such as gas evolution, self-discharge of positive electrode, poor Coulombic efficiency and poor cycle life.[2] To avoid the adverse effect of VC on the LNMO electrode, VC is fixed on graphite surface via chemical bonding in this work. The surface-bonded VC is decomposed to play the beneficial roles on the graphite electrode, but does not have harmful effects on LNMO electrode because VC cannot move to the positive electrode.

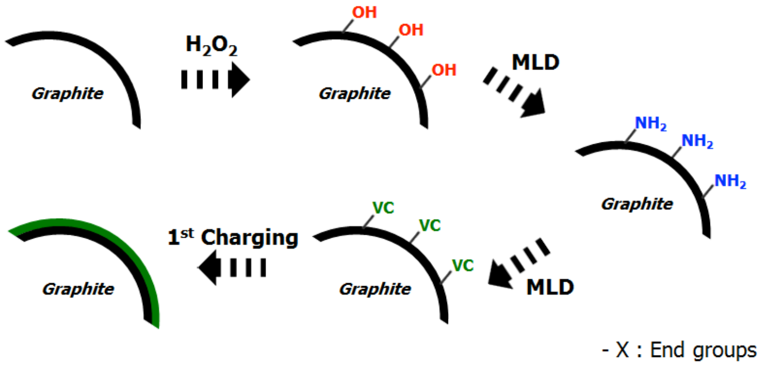

Fig.1. Schematic diagram for attachment of VC on graphite electrode

VC is fixed on the surface of natural graphite (DAG87) by using the molecular layer deposition (MLD) method, the detail of which is presented in Fig. 1. Upon the first charging, the surface-bonded VC decomposes to generate a SEI layer and the as-generated SEI layer plays its own roles, one of which is the prevention of additional electrolyte decomposition. Moreover, the detrimental effects such as gas evolution are not found on the LNMO electrode, obviously due to the confinement of VC on the negative electrode.

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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.

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

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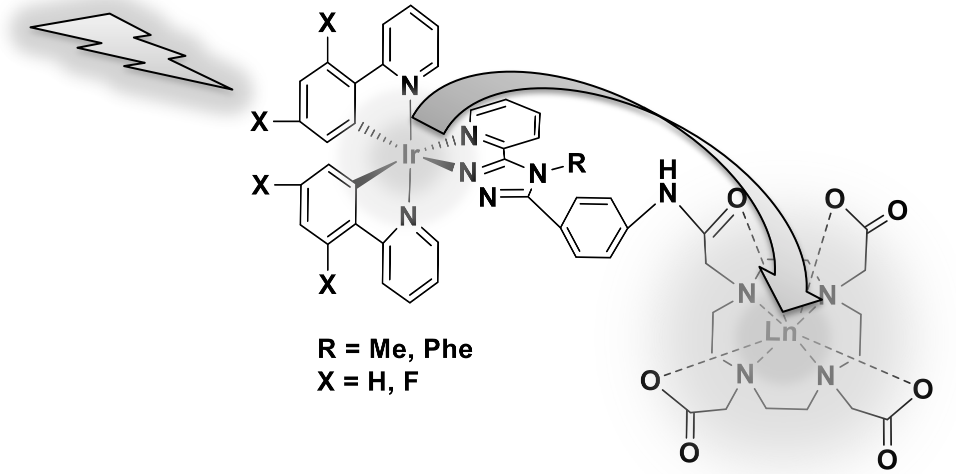
Lanthanide's luminescent f-f excited states give very characteristic emission profiles (distinct for each lanthanide ion). The forbidden f-f transitions require sensitizing by "antenna" groups to generate the lanthanide excited state.[1] Electrochemiluminescence (ECL) is a powerful alternative to traditional 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-tetraazaccyclododecane-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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Effects of Electrolyte pH on the Inherent Electrochemistry of Layered Transition-Metal Dichalcogenides (MoS_2, $MoSe_2$, WS_2, WSe_2)

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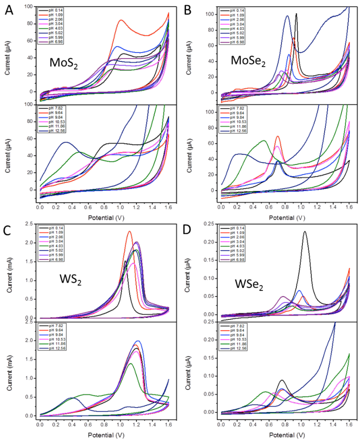
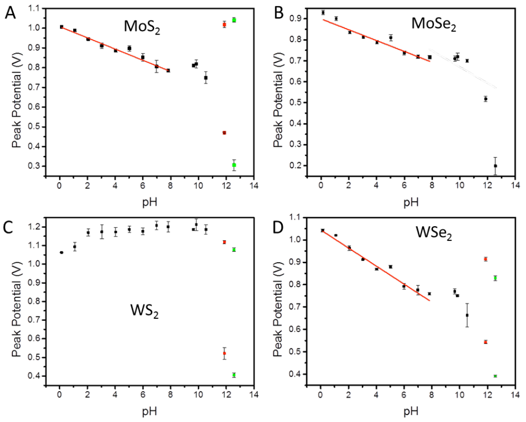
The research into transition-metal dichalcogenides (TMDs) has been gaining widespread interest recently as they are found to exhibit great physical and chemical properties. Potential uses of these materials include capacitors, energy storage devices and sensing platforms. However, despite these potential uses, the operational capabilities of TMDs are limited by the inherent electrochemistry of these materials. Inherent electrochemistry refers to the changes observed in the properties and characteristics of the material when used as an electrode surface. These TMDs may undergo redox reactions at certain potential ranges which will limit its capabilities especially in the sensing and biosensing application. Several factors have been found to affect the inherent electrochemistry of TMDs such as temperature and pH. In this research, we investigated the changes in the inherent oxidative peaks of different TMDs, namely MoS_2, $MoSe_2$, WS_2, and WSe_2, at different electrolyte pH values. This perimeter was chosen as it is an important factor for the optimization of buffer system that can be easily manipulated and optimized as compared to other factors.

Changing the pH of the electrolyte was found to influence and affect the inherent oxidation of TMDs, more noticeably the peak position. This could be attributed to the different reaction mechanisms and stability at the different pH values. An increase in the electrolyte pH from 0 to 8 shows a linear decrease in the peak potentials of the inherent oxidative peaks. However, small changes in peak potentials were observed at low alkaline pH levels (from 8 to 11). Beyond pH 11, the emergence of an additional peak at low potentials, apart from the inherent oxidative peak, was observed for most of the TMD materials studied. This insight into the pH dependence of the oxidation of TMD materials is of paramount importance for their electrochemical applications. WS_2 showed an almost similar peak position and relative stability over the pH range of 2–12. Moreover, tungsten-based dichalcogenides exhibited relative kinetics stability, owing to almost consistent peak heights, as compared to molybdenum-based dichalcogenides.





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Light scribe graphene and conducting polymers for generating a new, high-performance electrochemical electrode

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The combination of polymer science and nanotechnology shows great potential for generating variable devices of sensors and actuators. Conducting polymers (CPs) have polyconjugated structures with electronic properties similar to metals, while remaining properties of conventional organic polymers. The most well investigated CPs involve polypyrrole (PPy), Poly (3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI), polythiophene (PTs) and poly(phenylenevinylene) (PPV). Several CPs have been widely used in biosensor design because of their good conductivity, surface properties, biocompatibility and electrochemistry. Firstly, we investigated DNA sensing using pyrrole and functionalized pyrrole copolymer transducer. We polymerized polymer on the standard and commercial glassy carbon electrode. The sensing results were expressed by electrical impedance spectroscopy.

Considering as a promising future material, graphene shows several excellent properties. Particularly due to its large surface area and high conductivity, graphene is highly expected as a promising candidate to fabricate a high-performance electrode. As a new member of graphene family, light scribe graphene (LSG) has been demonstrated promise in fabrication of super capacitors, gas sensors and recently strain sensors. However, these devices were usually tested LSG in solid state or organic electrolyte. The pristine LSG electrode usually breaks in aqueous solution because graphene oxide is soluble in water. In this way, we aim to create LSG based electrode with improved stability and electro catalytic activity in aqueous solution. In this work, we prepared graphene oxide/ PVDF-HFP composites with different polymer ratio. We used a DVD burner to light scribe the composites after deposition and applied these LSG/PVDF-HFP as distinct electrodes. The electrochemical performance of LSG/PVDF-HFP electrodes was expressed by cyclic voltammetry and electrical impedance spectroscopy, with inner and outer sphere redox couple in electrolytes. The LSG/PVDF-HFP electrodes showed high stability in electrolyte and demonstrated fast heterogeneous electron transfer rate. Furthermore, we electro-polymerized a layer of PPy on the surface of LSG/PVDF-HFP electrodes. It also showed some interesting electrochemical properties. Look forward, the LSG/PVDF-HFP electrodes were porous, robust and fast to fabricate. These LSG based electrodes could demonstrate the potential in the applications of electrochemical bio-sensing and flexible lithium ion batteries.

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 $Ru(bpy)_3^{2+}$ 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 µM and 17.82 µM 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].

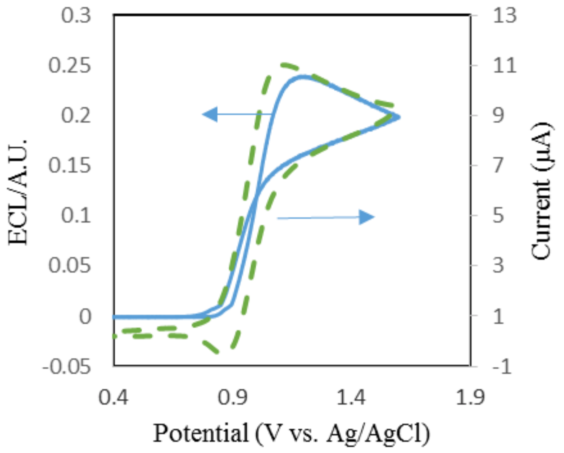

Fig 1. Response for 1mM $Ru(bpy)_3^{2+}$ solution in presence of PSE 1mM in pH 10 phosphate buffer.

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Reduced Graphene oxide improve the performance of glassy carbon electrodes against DNA and NADH detection

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Graphene, a two-dimensional carbon lattice, has been attracting much attention in the field of electrochemistry. Graphene has a high theoretical specific surface area (2630 m^2g^{-1}) and excellent electron conductivity, being a great candidate for electrochemical applications, such as fuel cells, supercapacitors, batteries and electrochemical sensors[1,2].

We recently published a comparative study about the electrochemical response of GC electrode modified with oxidized and non-oxidized multiwalled carbon nanotubes, graphene oxide (GO) and chemically reduced GO (C-RGO) against dsDNA[3]. Our results showed that the type and degree of oxidation have a strong effect on the electroactivity of the modified electrode. GCE/C-RGO clearly exhibited the most electroactive surface among the carbon nanomaterials, demonstrating that the graphitic structure is highly important. A more sensitive electrochemical response against dsDNA was obtained when GCE/C-RGO electrode was used.

In this work we present the results obtained using modified glassy carbon electrode with electrochemical reduced graphene oxide (E-RGO) on the electrochemical response against single strand DNA (ssDNA) and NADH.

The ss-DNA immobilization was achieved through immersion of the modified electrode in a stirred solution containing ss-DNA. The response of ss-DNA was evaluated through the oxidation of guanine measured by differential pulse voltammetry (DVP). In the case of NADH the electrode was modified with GO and then a potential was applied to reduce it to form the E-RGO *in situ*. The response of NADH was then evaluated using amperometry.

E-RGO was characterized by Raman and X-ray photoelectron spectroscopic showing an inverse correlation between the amount of oxygen in the sample and the degree of graphitic defects. Also a great capacitance was observed. For both analytes an increase on the sensitivity was obtained using E-RGO instead GO and the resulting modified electrodes show a reproducible response. In conclusion, the reduction method introduces larger defects and less oxygen function on GO which produce an improvement in the electroanalytical response.

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Porous Carbon Electrodes for Non- and Faradaic Reactions

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Carbons are nowadays playing a crucial role in many areas of electrochemistry such as capacitive deionization, redox reactions, oxidation and reduction. Porous carbon electrodes become one of the most applicable materials due to their electrochemical stability, cost, high surface area, etc. Most of all, the high electro-active surface of the porous carbon electrode is one of main advantages in non- and/or Faradaic reactions. All the electro-active species access the surface through the cumulative resistance of the electrolyte inside the pore. Thus, the controlling technology to have various pore structure with a wide range of pore size. For non-Faradaic reactions, much attention has been being paid to the fabrication of meso-porous carbon electrodes due to less resistance to access to adsorption surface with less activation energy. For Faradaic reactions, porous carbon electrodes with less activation overpotential is preferred to be functionalized by introducing electron donating or accepting species to the carbon surface. In this study, for non-Faradaic reactions, the mixture of carbons with different particle sizes were used to fabricate porous carbon electrodes to increase the fraction of meso-size pores. In addition, for Faradaic reactions, nitrogen-doping porous carbon electrodes were developed to decrease activation overpotential for oxygen reduction reactions with the type of surfactants. It was confirmed for both the porous carbon electrodes in terms of Raman, SEM, various voltammetry methods, porosimeter, etc.

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

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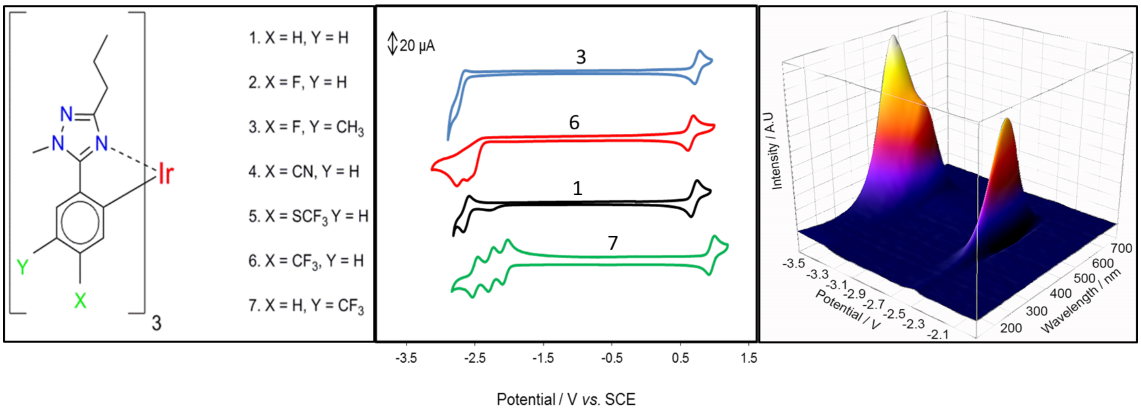
The spectroscopy, electrochemistry and electrochemiluminescence (ECL) of a family of blue emitting homoleptic cyclometalated complexes based on *fac*-tris(5-aryl-1,3-disubstituted-[1,2,4]triazolyl)iridium(III) have been investigated. The effect of varying the substituents on the phenyltriazole unit is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



All the complexes are blue-green emitters, showing high photoluminescence efficiencies (ϕ_{PL} ~ 0.60-0.97) with a single-exponential luminescent lifetime in the range of (1.81 – 3.49) µs. 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 Ir(III) / Ir(IV) redox couple while chemically reversible reductions have not been observed except for the complex with a (-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 $Ru(bpy)_3^{2+}$ (bpy=2,2'-bipyridine) (ϕ_{ECL} ~ 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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Immovilization of Cyclodextrin on Gold Electrode Based on Bottom-Up Approach

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Cyclodextrins (CDs) are organic macrocycles which possess a hydrophobic toroidal cavity and therefore are capable to form inclusion complexes with hydrophobic molecules of compatible size. Based on the encapsulating properties of cyclodextrins (CDs), they are an attractive group used as modifier of surfaces Attachment of these host molecules on surfaces is an important research topic. The most common strategy is the chemisorption of thiolated CDs on gold surfaces with long alkyl as spacers to obtain self-assembled structures. However, the incorporation of the alkyl chains creates an insulating layer that hampers their use in applications based on electron transfer processes.

The purpose of the present work was to immobilize amino β-CD on gold surfaces by bottom-up approaches and to study both the effect of the sublayer used as platform for the immobilization and to evaluate the influence of the number of amine terminal groups present in the β-CDs structure. Immobilization of amino β-CDn (with n=1, 2 or 7 amine groups on the primary rim) at the gold surfaces was carried out employing different methods: 1) by direct adsorption, 2) by amide bond formation with the carboxylic groups of a self-assembled monolayer of 4-mercapto aminobenzoic acid (MBA) and 3) by amide bond formation with the carboxylic groups of the electro-grafted diazonium salt synthesized in situ from 4-amine benzoic acid. Each method was followed using electrochemical measurements, cyclic voltammetry, and surface plasmon resonance using different redox probes: hydroquinone, ferricyanide and ferrocene methanol. Chemical and electrochemical treatments were used to prepare gold surfaces. Electrodes with roughness factor of 2.3 ± 0.4 were employed.

The results indicate that the increase of amine groups favors the direct adsorption process. The multivalent exposure of amino moieties allows stable adsorption. MBA was quimisorbed on gold; then the coupling between carboxylic group of MBA and amine terminal group of β-CDn was carried out using N-hydroxysulfosuccinimide (NHS) and N-(3-Dimethylaminopropyl)-N′-ethylcarbodimide. Using this methodology, the amount of cyclodextrin adsorbed not increases proportionately to the number of amino groups this could be related to steric effect for the formation of chemical bound or to the formation of multilayered structures.

We found that the highest changes are obtained using electrografting of diazonium salt where amino β-CDn are immobilized in higher amount on the surface than using MBA. Additionally, the amount of immobilized β-CD_2 and β-CD_7 are higher than β-CD_1. The presence of 2 or more amino terminal groups on the primary rim of β-CDn allows a greater number of couplings, although the steric hindrance slightly disfavors immobilization of β-CD_7.

Our results indicate, at least initially, a higher surface coverage was obtained using β-CD_2 although the orientation of the β-CD core may be not adequate to permit the inclusion. Nevertheless, the sensitivity of the redox probes to the surface chemistry can be affected by factors such as presence of oxides, hydrophobic effects, among others, it is clear that the immobilization of β-CD_2 affects more the electron transfer of both hydroquinone and ferricyanide.

Acknowledgements
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Polymer Brushes Grafted Conjugated Polymers for Biomedical Applications

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Grafting of polymeric side chains onto conjugated polymer backbones provide a versatile route towards designer conjugated polymers with added functionality, tunability in their optoelectronic properties, processability and responsiveness to stimuli. In our previous work with charged brushes, we have demonstrated a potential-dependent switch[1,2]. In this presentation we will discuss polymeric brushes grafted from conductive polymer films which display dynamic surface switching dependent on either pH [3], or salt, temperature and electrode potential[4]. Such surfaces present novel and exiting biointerfaces with multiple control parameters, with a range of additional possible applications, such as in micro- and nanofluidics and chromatography separation.

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Fast Responsive and High Performance PPy-PEO Conductive Polymer Actuators

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Polypyrrole (PPy) has been extensively studied as an actuator as it shows significant dimensional changes leading to swelling and shrinkage when it is oxidised or reduced. Improving the physical, chemical, electrical and mechanical properties of the PPy is of great significance in order to achieve fast responsive and high performance actuators for state of art applications like artificial muscles, robotics and micro-electromechanical devices.

In this study, we report the electro-chemo-mechanical deformation of the PPy films doped with dodecylbenzenesulfonate (DBS) in the presence of, polyethylene oxide (PEO) under isometric (constant force) conditions. The PPy-PEO composite films, at different compositions of PEO were actuated in propylene carbonate electrolyte (0.2 M lithium bis-trifluoromethanesulfonimide) and a remarkable 15% of mixed (both cation and anion) actuation was observed in the film containing 15 wt% PEO. The cation driven actuation was favoured by the ingress of Li^+ cations to compensate the immobile DBS^- anions while $TFSI^-$ anions contributed for the anionic actuation. The concentration of PEO was varied from 5 wt% to 20 wt% in order to determine the optimum amount of PEO, making the PPy-PEO film produce fast as well as better performance. The performance of the PPy-PEO films was improved with the increase in the amount of PEO marking 15 wt% the optimum amount. The strain degraded for the higher concentration of PEO above 15 wt% making the film behave as an insulator interfering the ions movement. The ECMD results indicated mixed actuations for all the PPy-PEO films where the cation driven actuation dominated the anion driven actuation due to more favorable movement of Li^+ cations rather than $TFSI^-$ anions provided by the incorporation of PEO in the backbone of PPy.

The presence of PEO in the PPy films was confirmed by the SEM-EDX measurements. Increase in the granular size in the PPy films and higher carbon/nitrogen (C/N) ratios were the clear evidence revealing the presence of PEO in the polymer films. In the future, we aim to obtain electrically stable PPy-PEO which can maintain consistent actuation characteristics even after continuous cycling for realistic applications.

Enhanced Mechanical Strength of Gold Electroplating Materials Fabricated by Multi-Layer Structure

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Gold materials have been applied in electronic devices due to the high chemical stability and electrical conductivity. In a recent study, an accelerometer utilizing CMOS-MEMS (complementary metal-oxide-semiconductor-micro-electrical-mechanical system) has been developed by gold electroplating materials that is fabricated by post-CMOS process [1]. The sensitivity of the gold-based accelerometer is higher than that of conventional silicon-based accelerometers mostly because of the high density of gold [2]. Meanwhile, there is a concern in applications of gold materials as movable structures in electronic devices since gold material, which has strength in the range of 180 MPa [3], is known to be a soft metallic material. It is important issue to investigate the mechanical strength of the gold electroplating material from the view point of fabrication process and mechanical structure. Moreover, we have developed the method to enhance the mechanical strength of gold electroplating material.

Electroplating is an attractive method to fabricate electronic devices because it is inexpensive and easy method without strict temperature control. We could predict the possibility to enhance the mechanical strength of the electroplated materials by refining the grain size through the control of the electroplating conditions. This is because mechanical strength of metallic materials is increased with a decrease in the grain size based on Hall-Petch relationship [4]. In fact, the fabricated gold device would be treated by the temperature of the fabrication process [1,2]. As a result, the heat treatment process could lead to severe grain growth and a decrease in the mechanical strength.

In this study, in order to enhance the mechanical strength, we have investigated a multi-layer gold material structure which consists of several Ti/Au layers. Here, Au involves electroplated gold layer on seed gold layer. Ti is used as adhesive layer. The multi-layer gold structure was fabricated on a silicon dioxide substrate. After the silicon oxide deposition, a layer of titanium was evaporated to be used as an adhesive layer and a seed layer of gold was evaporated on the titanium layer. Then, a single Ti/Au layer was repeatedly formed several times to realize the multi-layer structure. After the each Ti/Au layer process, annealing at 310ºC was performed except for the final layer. The multi-layer structure was fabricated by six layers of Ti/Au, where the number of the Ti/Au layers means the maximum layer number in the fabrication process. In order to evaluate the mechanical strength of the multi-layer structure, compression tests using micro-pillars having the multi-layer structure were carried out. The micro-pillars were fabricated by focus ion beam milling having dimensions of $13 \times 13 \times 42\ \mu m^3$.

Compression tests show that the mechanical strength reaches 300 MPa. In conclusion, we could confirm that the multi-layer gold structure has a potential to enhance the mechanical strength of gold electroplating material.

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Molecular Solvation Theory of Electric Interfacial Layer in Nanosystems

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Ornstein-Zernike type integral equation theory of liquids is becoming increasingly popular, as it enables predictive microscopic modelling of chemical species, nanoparticles, and biomolecules in solution. In particular, the 3D-RISM-KH molecular theory of solvation[1-3] yields 3D maps of correlation functions of solvent molecules site at a solute (supra)molecule or nanoparticle and then solvation free energy (SFE) analytically. With an input of a classical molecular force field of interaction potentials between explicit solute and solvent molecules (same as in molecular simulation), it accurately predicts the solvation structure, SFE, and electrochemistry of chemical and biomolecular species in solution and soft matter.[1-5]

The 3D-RISM-KH theory has been applied to evaluate the solvation structure, thermodynamics, and electric interfacial layer of modified cellulose nanocrystals (CNC) in ambient aqueous NaCl solution at concentration 0.0–0.25 mol/kg.[4] The MD relaxation induces a right-hand twist in CNC and rearranges its initially ordered structure with a macro-dipole of high density charges at the opposite faces into small local spots of alternating charge at each face. This surface charge rearrangement observed for both neutral and charged CNC significantly affects the ions distribution around CNC in aqueous electrolyte solution. The SFE of charged sulfated CNC has a minimum at a particular electrolyte concentration depending on the surface charge density, whereas the SFE of neutral CNC increases linearly with NaCl concentration. The SFE contribution from Na^+ counterions exhibits the behavior similar to the NaCl concentration dependence of the whole SFE. Analysis of the 3D maps of Na^+ density distributions shows these model CNC particles exhibit the behavior of charged nanocolloids in aqueous electrolyte solution: an increase in electrolyte concentration shrinks the electric interfacial layer and weakens the effective repulsion between charged CNC particles. The 3D-RISM-KH method readily treats solutions of a given composition to predict effective interactions between CNC particles, and provides structural models and modeling procedure to study effective forces and phase ordering of CNC suspensions in electrolyte solution.

Further, the 3D-RISM-KH theory was employed to study and validate against experiment the molecular recognition between kaolinite clay and a series of heterocyclic aromatic compounds (HAC) representative of N- and S-containing moieties in bitumen asphaltene macromolecules in toluene solvent.[5] From the 3D site density distributions, SFE, and 3D-SFE density, 3D-RISM-KH predicts the arrangement and thermodynamics of adsorption of HAC and toluene on the kaolinite surface. Spectrophotometric measurements show that among the HAC studied, only acridine and phenanthridine adsorb quantitatively on kaolinite. For these pyridinic HAC, the adsorption curves fitted to the Langmuir isotherm in the monolayer domain indicate a good homogeneity of the first layer. 3D-RISM-KH predicts the aluminum hydroxide surface of kaolinite is preferred for HAC adsorption due to strong hydrogen bonding with the pyridinic N atoms, while the rest of HAC adsorb weaker. Adsorption on the silicon oxide side is weak and delocalized, as evident from 3D-SFE density. Toluene sites effectively compete for kaolinite surface with non-hydrogen bonding HAC such as fused thiophenes. The adsorption enthalpy and loading ratio of phenanthridine-acridine are calculated and correlated to experimental Langmuir constant and adsorption loading. This provides insights into the specific interactions of clays, bitumen, and solvents components.

Finally, the replica RISM-KH-VM molecular theory of solvation in nanoporous material is used to reveal the mechanism of sorption and electrochemistry of electrolyte solution in nanoporous electrodes.[2,3] It is drastically different from a planar electrode interface due to substantial distortion electric interfacial layer of electrolyte ions and solvent molecules by nanoporous confinement and surface functionalities. The method predicts solvent-specific wetting and water depletion in hydrophobic nanopores, asymmetry in solvation and adsorption of cations and anions, desalination in hydrophobic nanopores and its reversal with external voltage, and specific adsorption in functionalized nanopores. The method reveals that specific capacitance of nanoporous electrodes is determined by a chemical balance in the Nernst-Planck equation, including the potential drop across the Stern layer at the surface of nanopores and the Gouy-Chapman layer averaged thermally and statistically over the nanoporous material, the osmotic term due to a difference in the ionic concentration in the electrodes and bulk solution, and the chemical potentials of sorbed solvated ions statistically averaged over the nanoporous material.

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In situ IR, XAS and ESMS-based studies of electrically polarized nickel, copper and gold electrode systems with pseudohalide ions (CN^-, NCO^-, NCS-, NCSe-, and NCTe-) in neat DMF and DMSO electrolytes, featuring aspects of electrocatalysis, electrode modification and sensing

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A review[1-5] is provided of subtractively normalized interfacial Fourier transform infrared (SNIFTIRS), X-ray absorption(XAS) and Electrospray mass spectrometry (ESMS) studies of the electrochemistry of the interaction of “pseudohalide ions”, i.e. cyanide ion or ions containing the nitrile group with attached chalcogen atoms (i.e. –O, -S, -Se, and –Te) , with electrically polarized nickel, copper and gold electrodes in neat dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) electrolytes. 0.1 mol L^{-1} tetrabutylammonium perchlorate functioned as the inert supporting electrolyte in the 0.025-0.050 mol L^{-1} pseudohalide ion/DMSO or DMF solutions used. Potential ranges varied from -1500 mV(AgCl/Ag) to +2000 mV(AgCl/Ag). The use of the cyano/nitrile-based species in the electrolytes allowed detection of the electrogenerated products containing these moieties in an IR spectral window of 2400-1900 cm^{-1} where no fundamental IR stretching bands from the solvents used occur. The potentiometric behaviour and molecular speciation observed by SNIFTIRS indicated a range of processes was occurring on the electrodes studied, namely 1) solvent adsorption, 2 electrodissolution of the metal electrodes to form complex ion species incorporating the pseudohalide ions, 3) insoluble film formation and passivation, 4) gas evolution, decomposition ($TeCN^-$) to form films which modified the electrode surface and affected the electrochemistry accordingly, and 6) electrocatalytic processes enhancing the electrooxidation of cyanide ion to $CO_{2(g)}$. Synchrotron based XAS studies using X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption fine structure (EXAFS) techniques were used to elucidate the coordination geometry of the Ni-isocyanato, isothiocyanato and isoselenocyanato complex ions detected by the SNIFTIRS investigations of the electrically polarized Ni electrodes in the DMSO-based electrolytes containing these pseudohalides. In the case of electrically polarized Cu electrodes, XANES spectra demonstrated the importance of the Cu(I) oxidation state as an electrogenerated species in the DMSO based electrolytes. SNIFTIRS investigations involving interaction of the tellurocyanate ion with Ni, Cu and Au electrodes represented the in situ IRinvestigation using this unstable ion and showed in all electrodes monitored that the tellurocyanate ion decomposed to form a layer of Te on the electrode and cyanide ion which interacted to a limited extent with the modified Te-coated electrode surfaces to form metal-cyano complex ions The sensitivity to decomposition of the $TeCN^-$ ion to polarizing cations was found via SNIFTIRS investigations to hold some potential as a sensor to the presence of positive metal ion species forming on the electrode.

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Glucose oxidation at stochastic nanoparticle electrodes: gold nanoparticles produced by laser ablation

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There are many examples of nanoparticles in everyday materials that can expose humans to inorganic and organic (including biological) nanoparticles, some of which are or might be toxic, e.g. sunscreen, clothing, motor exhaust fumes, volcanic ash. While much work is undertaken to study the toxicity of nanoparticles, these studies require complex experimental bio-assays and are unsuited to an everyday, routine test to determine whether a sample contains nanoparticles. The electrochemical behavior and detection of nanoparticles via interaction with an electrode surface has become an area of intense activity since initial reports by Bard and co-workers and Compton and coworkers. For example, Bard and colleagues showed the ability to detect nanoparticles by linking electrocatalytic reactions at nanoparticle surfaces with impact on an inert electrode, whereas Compton and colleagues employed nanoparticle deposition and stripping approaches to achieve detection.

In this work, the electrochemical behavior of gold nanoparticles produced by the Laser Ablation Synthesis in Solution (LASiS) method was studied. The LASiS method is highly flexible and enables production of nanoparticles coated with desired capping agents that are present in solution during the ablation process. In preliminary studies, gold nanoparticles produced in pure water were examined by cyclic voltammetry and chronoamperometry. The presence of gold nanoparticles dispersed in solution was detected by the electrocatalytic oxidation of glucose in alkaline solution. At constant applied potential, gold nanoparticles randomly impact on a carbon fibre electrode and catalyze the oxidation of glucose. This produces current spikes (Fig. 1). In the absence of gold nanoparticles, glucose oxidation does not occur on the carbon electrode. Accordingly, the nanoparticles dispersed throughout the solution behave like a stochastic array of disconnected nanoelectrodes. Their impact on the electrode provides the electrical connection that enables electrochemical reactions to be driven and monitored. This opens up scope for nanoparticle detection, for which the latest results will be presented and discussed.

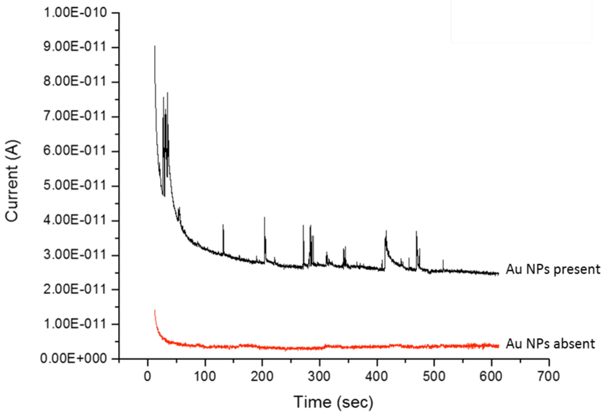

Figure 1. Chronoamperometry of gold nanoparticle impacts on a carbon fibre microelectrode in alkaline glucose solution.

Generation of nanoreactors at electrocatalytic interfaces: controlled distribution of distinct noble metal sites within nanostructured mixed-metal oxide supports

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There has been growing interest in small organic molecules (as alternatives to hydrogen) for application in low-temperature fuel cells. Such organic molecules as formic acid, methanol, dimethyl ether or ethanol can be ideally oxidized to carbon dioxide. But realistically the reactions are rather slow at ambient conditions. Obviously, there is a need to develop novel electrocatalytic materials.

Platinum-based nanoparticles have been recognized as the most active catalytic systems towards oxidation of ethanol at low and moderate temperatures. Simple Pt anodes are readily poisoned by the strongly adsorbed intermediates, namely by CO-type species, requiring fairly high overpotentials for their removal. To enhance activity of Pt catalysts towards methanol and ethanol oxidation, additional metals including ruthenium, tin, molybdenum, tungsten or rhodium are usually introduced as the alloying component. More recently it has been demonstrated that catalytic activity of platinum-based nanoparticles towards electrooxidation of ethanol has been significantly enhanced through interfacial modification with ultra-thin monolayer-type films of metal oxo species of tungsten, titanium or zirconium. Also gold in combination with platinum has been demonstrated to produce novel high performance bimetallic catalysts.

We explore here the concept of utilization of mixed metal oxide (e.g. ZrO_2/WO_3 or TiO_2/WO_3) matrices for supporting and activating noble metal nanoparticles (e.g. Pt, Pt-Ru, Pd, Ir or Rh) during electrooxidation of methanol, ethanol, formic acid and dimethyl ether. Remarkable increases of electrocatalytic currents measured under voltammetric and chronoamperometric conditions have been observed. The most likely explanation takes into account possibility of specific interactions of noble metals with transition metal oxide species as well as existence of active hydroxyl groups in the vicinity of catalytic noble metal sites. Among useful characteristics of metal oxides and related systems are the following: they can generate –OH groups at low potentials that induce oxidation of passivating CO adsorbates (e.g. on Pt); they can potentially break C-H bonds (e.g. by hydrogen tungsten oxide bronzes). When combined with dispersed Rh or Ir, they can possibly weaken C-C bonds during ethanol oxidation (e.g. through changes of the electronic properties of noble metals).

From Light-Emitting Bioswimmers to 3D Electrogenerated Chemiluminescence

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Electrogenerated chemiluminescence (ECL) is the phenomenon of light emission by the excited state of a luminophore produced upon an initial electrochemical activation.[1] The discovery of ECL emission in aqueous media has led to major applications in analytical chemistry, especially for sensitive immunoassays commercialized for clinical diagnostics.[2] ECL is thus a remarkably versatile method which offers many unique performances such as high sensitivity, extremely low background, high linear dynamic range, selectivity, stability of the luminophore, temporal resolution, and easy conjugation of the ECL-label to biomolecules. However, ECL emission is only generated at the electrode surface or in its immediate vicinity. ECL is by nature a 2D process, which is strictly confined to the surface of the electrode. This appears so far as an intrinsic limitation compared, for example, to chemiluminescence where reagents are mixed and react homogeneously to form the excited state in the bulk.

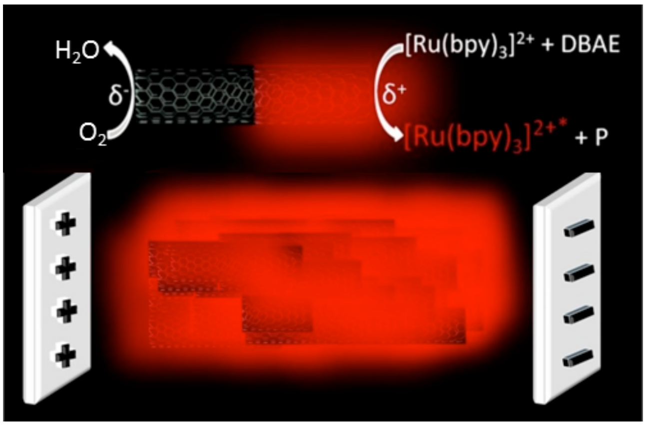

Figure 1. Principle of bulk ECL produced by a suspension of CNTs.

Bipolar electrochemistry (BPE) is a powerful wireless method which promotes electrochemical reactions at the extremities of conductive objects placed in solution when applying an electric field. It is an important method for a wide variety of applications, from analysis to materials science.[3] We exploited recently the versatility of BPE and its wireless characteristics to develop ECL-emitting bioelectrochemical swimmers.[4] Indeed, BPE induces simultaneously the production of gas bubbles for propelling the swimmers and enzymatic formation of the activated ECL reagents, which generate light only in the presence of glucose. Due to the wireless capabilities of BPE, we extended this idea from a single to thousands of conductive objects that were simultaneously addressed by this versatile technique.[5] Thus we demonstrated the efficient generation of bulk ECL (*i.e.* 3D ECL) at the level of a dispersion of conductive micro- or nano-objects in a capillary.[5] Indeed, each microbead or multi-walled carbon nanotube (MWCNT) is polarized by the electric field and ECL emission is therefore triggered in a wireless manner simultaneously on all objects to generate one or even two different colors.[6]

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Electrochemical Behavior of Fucoidan Extracts from Seaweeds at a Polarized Water-Organogel Interface

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Fucoidans belong to a class of sulphated polysaccharides derived from a variety of seaweeds and some marine invertebrates. They primarily contain α(1-3), or alternating α(1-3) and α(1-4), linked L-fucose components, with acetyl groups, sulfates or various branch points appearing periodically along the polymer chain [1]. With its numerous biological activities such as cancer treatment [2] and retrovirus inhibition [3], Fucoidans have been the interest of various studies and given its gamut of practical applications, a simple and direct detection method for measuring its presence is desirable, especially in complex sample matrices.

As an emerging viable detection technique for biomolecules, an assessment has been undertaken of the electrochemical characteristics of these polyelectrolytes at the interface between two immiscible electrolyte solutions (ITIES) [2]. This electrochemical approach offers the advantage of label-free detection of ionizable analytes which do not require being redox-active. Voltammetry and adsorption techniques were employed to study the Fucoidan extracts under different conditions: varying aqueous phase pH, scan rate, adsorption potential and adsorption times.

It was found that the voltammetric response was superior at pH 12, when the polyelectrolytes were mostly deprotonated. The polyelectrolyte (Fucoidan) structure varies amongst different seaweed species studied (Undaria and Fucus) which had a significant impact on the behavior of these extracts at the polarized water-organogel interface. This is in agreement with previous studies employing polyion-sensitive membrane electrodes [5]. Undaria showed a larger current response compared to Fucus at ~ 0.15-0.25 V, which can be attributed to the presence of more galactose units in its polymer backbone. Consequently, lower concentrations were measured for Undaria polyelectrolytes (50 μg/mL) while Fucus was detectable at 300 μg/mL using cyclic voltammetry. However, the application of an electrochemical pre-concentration step enabled the detection of lower concentrations (i.e. 20 μg/mL Undaria after only 60 s of electrochemical pre-concentration).

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

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The Role of Surface Species on Electrochemical Promotion of Catalysis

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Abstract

The optimization of selectivity and catalytic activity is crucial to obtain desired products. The catalyst for the electrochemically assisted catalytic reactor is chosen based on its ability to selectively enhance the reaction rate of certain products. The fact that the catalyst may consist of surface impurity or additional species may be introduced together with ionic promoter during spillover process such as shown in Fig. (1) is normally being neglected. There are only a few studies acknowledging this subject, thus we are still lack of understanding on the influence of such species to the catalytic activity and selectivity. Commonly the presence of surface species (impurity) became a concern when it has poisoning effect, but in some cases the surface species may also play a promoting role. An electropositive or electronegative element, for example, may act as structural promoter, thus have a synergistic effect with the spiltover promoter species to enhance the performance of the catalyst.

Figure

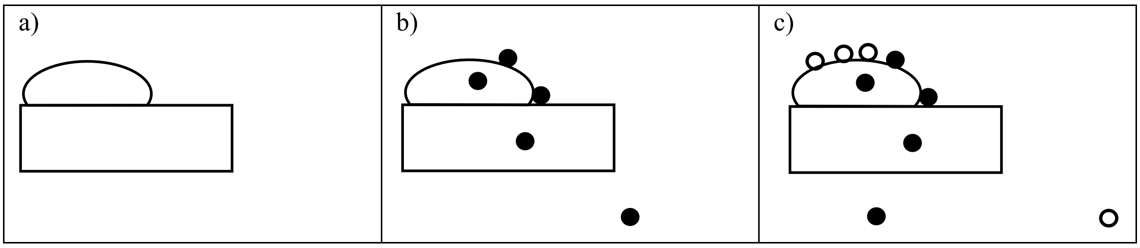

Fig.1. Schematic representation of catalyst deposited on solid electrolyte, (a) theoretical model assuming catalyst and solid electrolyte with no impurities; (b) laboratory model of catalyst and solid electrolyte with impurities; and (c) study model of catalyst with external deposition of impurities

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

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The detection of ammonia (NH_3) gas at low concentrations is of great importance due to its use in a wide range of industries i.e. oil and gas industry, fertilizer industry, refrigeration industry[1] 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) is 25 ppm in the gas phase. There are commercially available electrochemical gas sensors to monitor ammonia, mostly based on amperometric gas sensors (AGSs). However one problem with AGSs is that their solvent/electrolyte combinations are typically water/sulphuric acid, and can dry-up quickly, thus making the lifetime of these sensors very limited. Room Temperature Ionic Liquids (RTILs) have been attracting a great attention[2] as replacement electrolytes in AGSs due to their unique physical properties such as wide electrochemical windows, high intrinsic conductivity, low volatility and negligible vapor pressure, high chemical and thermal stability and their ability to dissolve a wide range of compounds. Importantly, they do not evaporate when exposed to a high gas flow, and can function in hot and dry environments. In our work, we are investigating new commercially available thin-film metal electrode surfaces, consisting 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) minimizes the overall cost of the sensor. A comparison of four different techniques will be employed for ammonia oxidation: linear sweep voltammetry (LSV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV), and potential-step chronoamperometry (PSC) over the concentration range of 10-100 ppm NH_3. The results on commercially available Pt thin-film electrodes, screen-printed electrodes, and microarray thin-film electrodes will be compared to “ideal” Pt microdisk electrodes. Calibration curves (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.

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A New Family of Perovskite Catalysts for OER in Alkaline Media: $BaNiO_3$, $BaNi_{0.83}O_{2.5}$

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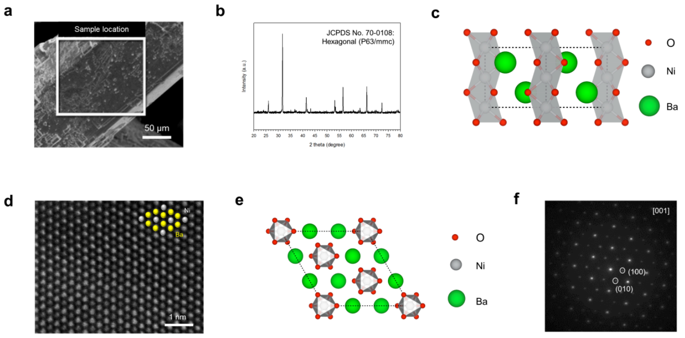
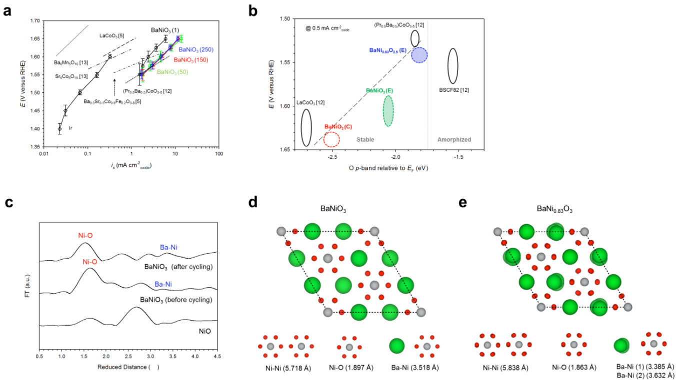
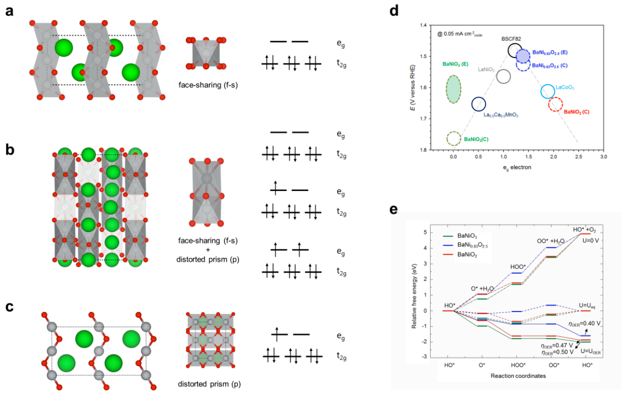
Establishment of sustainable energy society has been strong driving force to develop cost-effective and highly active catalysts for energy conversion and storage devices such as metal-air batteries and electrochemical water splitting systems. This is because the oxygen evolution reaction (OER), a vital reaction for the operation, is substantially sluggish even with precious metals-based catalysts. Here, we show for the first time that a hexagonal perovskite BaNiO3 can be highly functional catalyst for OER in alkaline media. We identify that the BaNiO3 performs OER activity at least an order of magnitude higher than an IrO2 catalyst. Using integrated density functional theory calculations and experimental validations we unveil the underlying mechanism is originated from structural transformation from BaNiO3 to BaNi0.83O2.5 (Ba6Ni5O15) over the OER cycling process.







Decoration of Liquid/Liquid Nanointerface Arrays with Silica for Visualisation of Diffusion Processes

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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 (nanoITIES) 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±6). The silica material modified the entire array at the closer-spaced pores (Figure 1Ba, r_c/r_a = 21±2), while individual pore modification by silica was observed at the widely spaced pores (Figure 1Bb, r_c/r_a = 91±7). This is attributed to the formation of overlapping diffusion zones at arrays with r_c/r_a = 21±2 or individual diffusion zones at the pores of the array with r_c/r_a = 91±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.

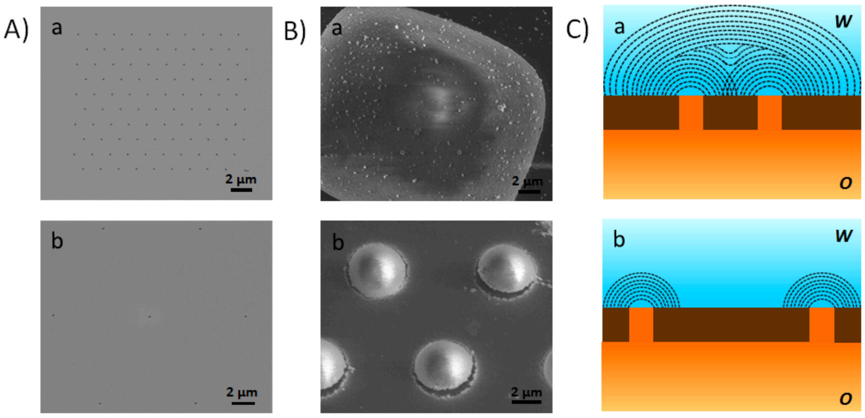

Figure 1. SEM images of the nanopore arrays with r_c/r_a of 21±2 (a) and 91±7 (b) before A) and after modification of silica materials B). C) Schematic views of their interfacial diffusion profiles.

Hg(II) ultra-fast trace determination using square-wave anodic stripping voltammetry on a glassy carbon electrode functionalized by a mixed diazonium/gold nanoparticles layer

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Mercury (Hg) is amongst the priority targets within the European Water Framework Directive [1]. This is mainly due to its wide release in the environment and to the bioaccumulation phenomena it gives rise to all along the trophic chain, thus being pernicious even from very low concentration. Thus, the need for cheap, compact and user-friendly sensors for Hg(II) trace level detection in natural water is a real challenge. In this context, electrochemical sensors appear to be an interesting alternative compared to spectroscopic techniques which require heavy and expensive devices. In particular, nanostructurated interfaces have received much attention [2].

In a previous work, we developed a sensor dedicated to Hg(II) trace detection based on gold nanoparticles (AuNPs) electrodeposited on a glassy carbon (GC) electrode. The resulting device allowed a very low limit of detection (LOD) to be reached, ca. 0.40 nM for 5 min Hg(II) preconcentration and a sensitivity of 0.23 µA nM^{-1} min^{-1} [3]. These latter results were further improved by including a chloride desorption step in the detection procedure, allowing a LOD of 19 pM to be reached with a sensitivity of 0.60 µA nM^{-1} min^{-1} [3]. However the sensor exhibited poor response stability due to the loss of active gold surface with time and electrochemical treatments.

In order to improve the stability of the sensor, an alternative strategy was investigated in this work. AuNPs were prepared by classical chemical route, namely the "Turkevich method", then filtered and deposited by physicochemical means onto GC surface previously functionalized by a diazonium layer. Two diazoniums bearing either nitro or thiol moieties as an anchoring group for the particles were used. In this talk, the functionalization procedure will be described together with the characterization of the AuNPs and the resulting diazonium/AuNPs interface by microscopic techniques (TEM, FEG-SEM). The stability of this interface will be also examined by cyclic voltammetry using hexaamineruthenium(III) as an electrochemical probe: 50 scans were then conducted without any change in the electrochemical signal. Finally, the results obtained with respect to Hg(II) trace detection will be presented. A particular focus will be given to the analytical performances of the sensor, which allowed very sensitive Hg(II) detection for the simple AuNPs interface with only 30 s preconcentration, thus affording an unprecedented ultra-fast Hg(II) trace analysis system.

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Ambient Temperature Prepared Amorphous Iron Phosphates as Hosts for Various Charge Carrier Ions

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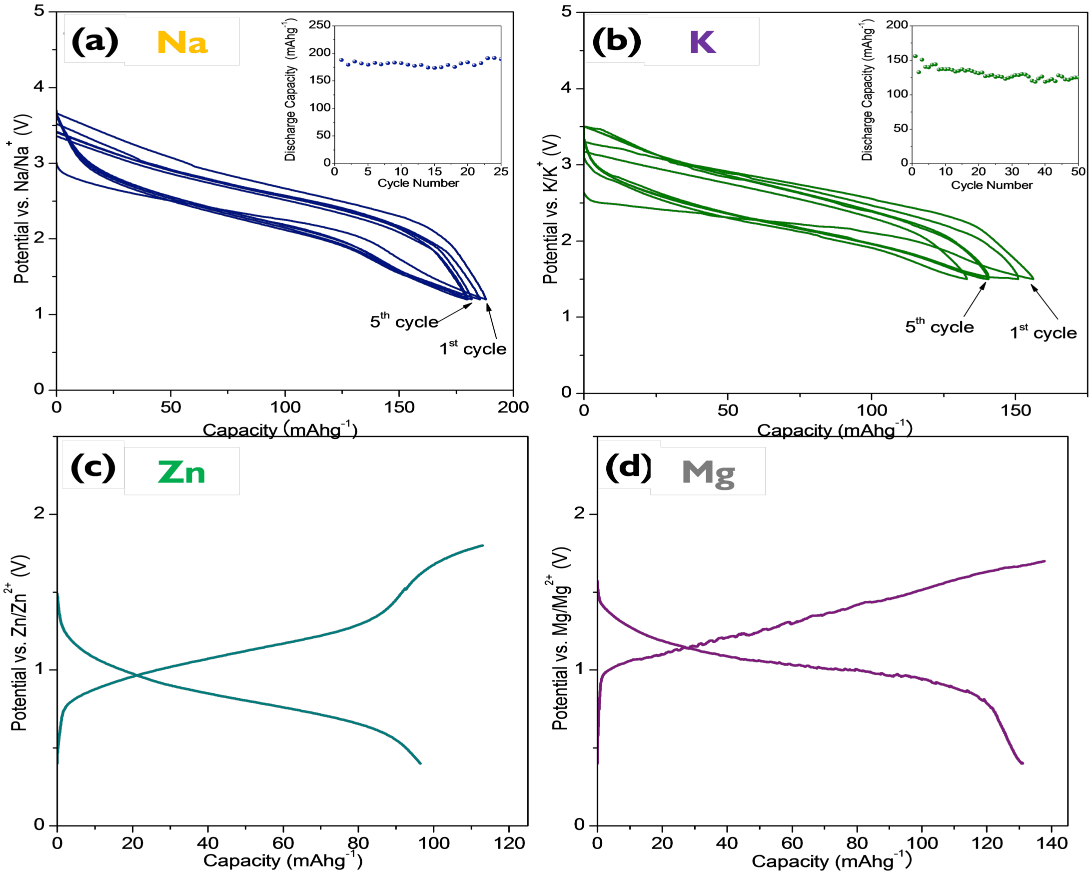
The global demand for electricity has increased twice as much as the demand for energy overall, and the demand for electricity is expected to further increase by more than two-thirds over the next 20 years. Energy storage/conversion technologies have therefore become a crucial research topic as we seek to make society sustainable. In particular, electrical energy storage is critical not only for supporting electronic, vehicular and load-leveling applications but also for efficiently commercializing renewable solar and wind power. In response to the ever-increasing global demand for viable energy-storage systems, sodium and potassium batteries appear to be promising alternatives to lithium ion batteries because of the abundance, low cost and environmental benignity of sodium/potassium. Electrical energy storage via ion-intercalation reactions in crystalline electrodes is critically dependent on the sizes of the guest ions. Herein, we report on the use of a porous amorphous iron phosphate synthesized using ambient temperature strategies as a potential host that stores electrical energy through the feasible insertion of mono-/di-/tri-valent ions. A combination of ex situ studies reveals the existence of a reversible amorphous-to-crystalline transition in this versatile electrode during electrochemical reactions with monovalent sodium, potassium and lithium. This reconstitutive reaction contributes to realizing specific capacities of 179 and 156 mAh/g versus sodium and potassium at current densities of 10 and 5 mA/g, respectively. This finding facilitates the feasible development of several amorphous electrodes with similar phase behavior for energy-storage applications.



Functionalization of electrochemical interfaces toward efficient solar energy conversion and catalytic reduction of carbon dioxide

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There has been growing interest in the development of photoanode materials for sunlight-driven oxygen generation (photoelectrochemical water splitting to oxygen and hydrogen). Among important issues is that the semiconducting oxide should be characterized by indirect optical transition in the visible part of the solar spectrum. We demonstrate here utility of gold nanoparticles (modified or stabilized with Keggin-type polyoxometallates, phosphomolybdates and their derivatized ruthenium analogues) to enhance photocurrents generated by mesoporous tungsten trioxide (pristine or structurally modified with polytungstates) photoanodes irradiated with visible light in aqueous solutions. To demonstrate generation of localized surface plasmons, we have performed measurements using scanning near-field optical microscope. The mechanism for the interaction between the gold plasmons, polyoxometallates and the semiconductor is complex but sound.

We also consider nanoelectrocatalytic systems that are of importance to the development of the effectively operating iodine-based charge relays in dye sensitized solar cells. The ability of palladium and platinum to induce splitting of I-I bond in the iodine (triiodide) molecule is explored here to enhance electron transfers in iodine/iodide redox couple. Following incorporation of Pt or Pd nanoparticles, charge transport has been accelerated within the triiodide/iodide-containing 1,3-dialkylimidazolium room-temperature ionic liquid. When both Pt nanoparticles and multi-walled carbon nanotubes have been introduced to ionic liquid system, a solid-type (non-fluid) electrolyte has been obtained. The dye-sensitized solar cell with this electrolyte has yielded reasonably high power conversion efficiencies (up to 7.9% under standard reporting conditions).

When it comes to the development of electrocatalytic systems for reduction of carbon dioxide, instead of conventional Pd (or Pt) nanoparticles, nanosized Pd (or Pt) immobilized within supramolecular assemblies of tridentate Schiff-base ligands or supported onto hybrid biofilm-based matrices have been considered. Reduction of carbon dioxide begins now at less negative potentials and is accompanied by significant enhancement of the CO2-reduction current densities. Among important issues are specific interactions between nitrogen coordinating centers and metallic palladium or platinum sites at the electrocatalytic interface.

Through intentional and controlled combination of metal oxide semiconductors, we have been able to drive effectively photo-electrochemical reduction of carbon dioxide. The combination of titanium (IV) oxide (TiO_2) and copper (I) oxide (Cu_2O) has been explored toward the reduction of carbon (IV) oxide (CO_2) before and after sunlight illumination. Application of the hybrid system composed of both above-mentioned oxides resulted in high current densities originating from photoelectrochemical reduction of carbon dioxide mostly to methanol (CH_3OH) as demonstrated upon identification of final products. The role of TiO_2 is not only in stabilizing the interface: the oxide is also expected to prevent the recombination of charge carriers.

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Comparison of Al Electrodeposition at Different Solvents

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Aluminum is used in many industrial fields such as semiconductor industry and electronic-/electric devices industry because of its light weight property, high conductivity and excellent corrosion resistance.

But, Al cannot be obtained from aqueous solutions since hydrogen evolution is dominant and so it has been electrodeposited from high temperature molten salts, organic solvents and ionic liquids. Organic solvent such as tetrahydrofuran (THF), ethers and dimethylsulfone ($DMSO_2$) are volatile at room temperature. Meanwhile, ionic liquids have some properties such as low volatility and good electrical conductivity, even though they show somewhat high viscosity at room temperature. Recently, glycol ethers

For Al electrodeposition, we used both 1-Ethyl-3-methylimidazolium chloride and diglymes as solvent. The main objectives of these different solvent was to compare the compactness and stability of Al deposits at different electroplating conditions. In some galvanostatic polarization and post-rinsing process treatment, Al deposits was changed porous and black surface morphology shortly after electroplating. We prepared Al electrodeposits by using various conditions of voltage/current application mode, solution temperature, agitation, electroplating time and different rinsing treatments. It was revealed that the combination of Al electroplating condition and post-treatment is essential for getting highly stable Al electrodeposited layers. We obtained Al electrodeposits of 20um thick at potentiostatic and galvanostatic polarization for 1hr.

Mechanical Properties of Chromium-Nanosized Diamond Particles Composite Electrodeposits

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Composite plating is a useful and low cost way to provide special surface properties, such as high hardness, abrasion and corrosion resistance, low friction coefficient to meet the requirements of advanced materials. According to the previous reports, it was found that introduction of nano-sized diamond particles to the chromium plating bath does not exert a great influence on the microhardness of chromium deposit.

So, the objective of our work was to study the properties of chromium composite plated with nano-diamond powders in order to contribute to development of chromium/nano-diamond composite plating. For this purpose, chromium matrix composite based on sulfate bath was made with nano-diamond powder by electrodeposition. The plating conditions for high wear resistance were current density of 60A/cm^2 and temperature of 50^{o}C. It was shown that the cross-sectional micrographs of chromium/nano-diamond composite plating layers displayed more cracks at higher thickness. It seems that lower current density increases the amounts of nano particles included in the deposits, but the distribution of nano particles was very random with clearly aggregated form, particularly in the vicinity of the cracks.

The wear resistance of chromium matrix composite with nano-diamond was 3-4 times higher than that of pure chromium deposit. The microhardness of chromium matrix composite was increased by the dispersion of nanodiamond particles in the deposit and reached to Hv.916 at 30 A/dm^2, 50^{o}C. The friction coefficient of chromium nano-composite was about 78% of pure chromium. In chloride medium, chromium matrix nano-composite is strongly passivated and its corrosion. resistance was manufested higher than that of pure chromium.

Comparison of Al Electrodeposition at Different Solvents

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A Tafel plot based investigation on the role of a capping agent during electrocatalysis of alcohols & polyols

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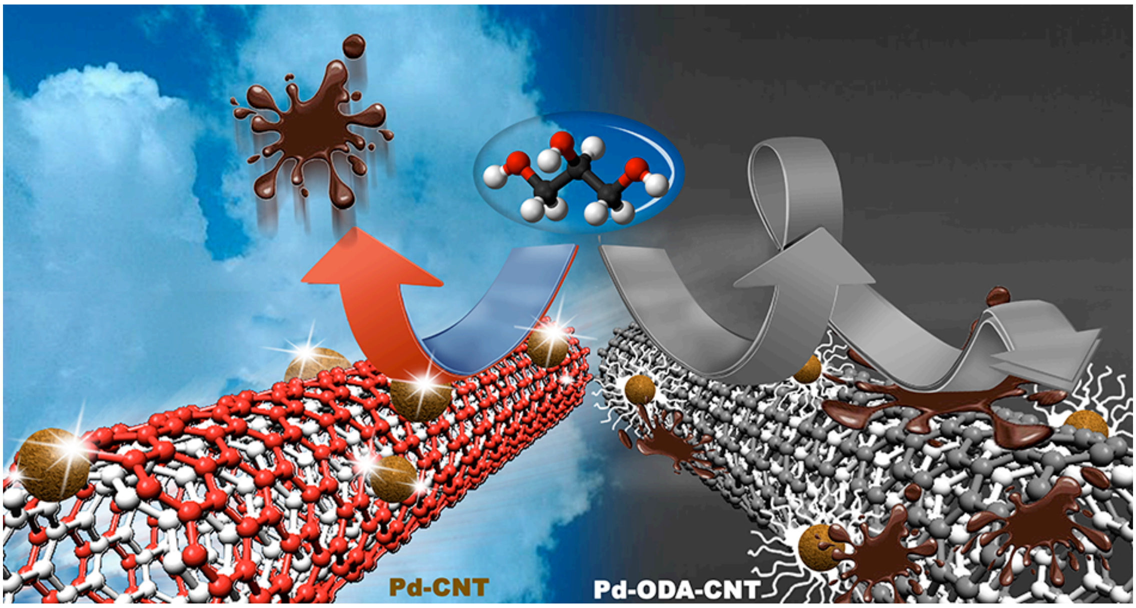

Electrooxidation of alcohols and polyols have received significant attention due to their promising application in low temperature direct alcohol fuel cells. The advantage of these fuel cells has been providing high energy density apart from having liquid fuels, thus enabling easy storage. Traditionally platinum is the most active catalytic material used in the fuel cells to enhance the electrooxidation rates. However, the major drawback associated with this technology been the accumulation of the carbonaceous intermediates on the electrocatalyst surface. This leads to blocking and also poisoning of the costly electrocatalyst, thereby reducing its catalytic activity. For the first time, in our study, it has been found that capping agents that are conventionally used to achieve precise control over the geometry and morphology of the nanocatalysts tend to show a relation towards the reaction intermediate accumulation.

In the present electrochemical investigation, the role of capping agent during electrocatalysis has been studied, vis a vis a detailed understanding on the reaction intermediate accumulation to the presence of the capping agents.

An electrochemical Tafel plot based model for electrooxidation reactions has been developed, to explain the fouling of an electrocatalyst surface due to the intermediates, in connection to the presence of capping agents. This understanding has been achieved with the use of Pd and Pt based electrocatalysts of choice, in the presence and absence of capping agent. This model has wide spread applications in accessing the stability and response of any electrocatalyst and thus serves as presumptive catalyst analysis prior to the use of catalysts in the fuel cells, thereby saving time and cost associated with the use of the material in alcohol fuel cells.

High Frequency Impedance Spectroscopy of Hydrogen Absorption in Thin Palladium Films Covered by Platinum Monolayers

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The hydrogen electrosorption in thin palladium films (50-1000 nm) was investigated at palladium electrodes covered by two-dimensional platinum deposits. The results for this model system show that the rates of the hydrogen sorption/desorption are orders of magnitude higher for platinized samples with respect to pure palladium. Hydrogen electrosorption is extremely fast, cathodic and anodic peaks are formed due to hydrogen absorption for 1000 nm thick Pd electrode (Figure - left) [1]. It should be noted, that the formation of similar peaks have never been observed for Pd films thicker than 10 nm.

Electrochemical Impedance Spectroscopy (EIS) has been used to determine the kinetics of the electrosorption processes at platinized Pd electrodes. This reaction is extremely fast and must be studied at high frequencies, inaccessible using the potentiostat. For this purpose a twin electrode configuration in a large frequency domain up to 1 MHz has been used [2]. Impedance between twin electrodes was measured directly using the frequency response analyzer (FRA). The resistance of the charge transfer was of the order of 0.02 Ω cm^2 (Figure 1 – Right). By means of EIS we have shown that the process is diffusion limited at platinized Pd layers. Diffusion coefficient, D_H, determined in EIS, is two orders of magnitude higher than that previously reported for thin palladium films. A distinct Warburg impedance has been observed for layers as thin as 50 nm (Figure 1 – Right).

The system stability after hydrogen absorption was assessed and the sorption mechanism will be discussed. Surprisingly high durability of the platinized palladium enables its use in a variety of applications where fast and selective response in the presence of hydrogen is required. The fundamental and practical relevance of the approach is related to the possibility of constructing novel hydride forming materials, which have only minute amount of overall platinum content and improved hydrogenation properties. This may indicate not only more efficient hydrogen storage, but also much higher power densities in case of hydride batteries.

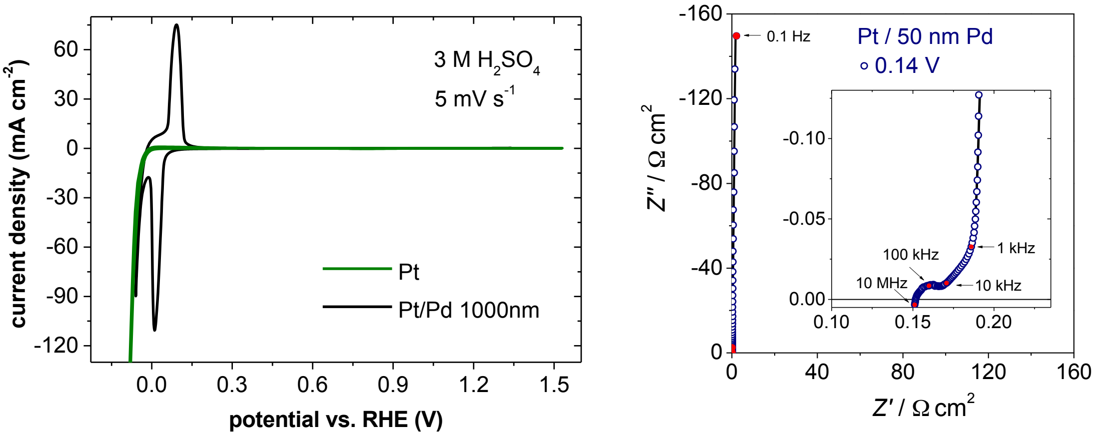

Fig. 1. (left) Cyclic voltammograms for Pt electrode (green line) and 1000 nm Pd covered by two Pt monolayers in 3M H_2SO_4 (black line) [1]. (right) Complex plane plot of impedance of 50 nm Pd electrode covered by one Pt monolayer measured in twin electrode configuration.

Literature
[1] P. Połczyński, R. Jurczakowski, J. Power Sources, 2016 in press
[2] B. Losiewicz, R. Jurczakowski, A. Lasia, Electrochimica Acta, **80** (2012) 292-301

High Frequency Impedance Spectroscopy of Hydrogen Absorption in Thin Palladium Films Covered by Platinum Monolayers

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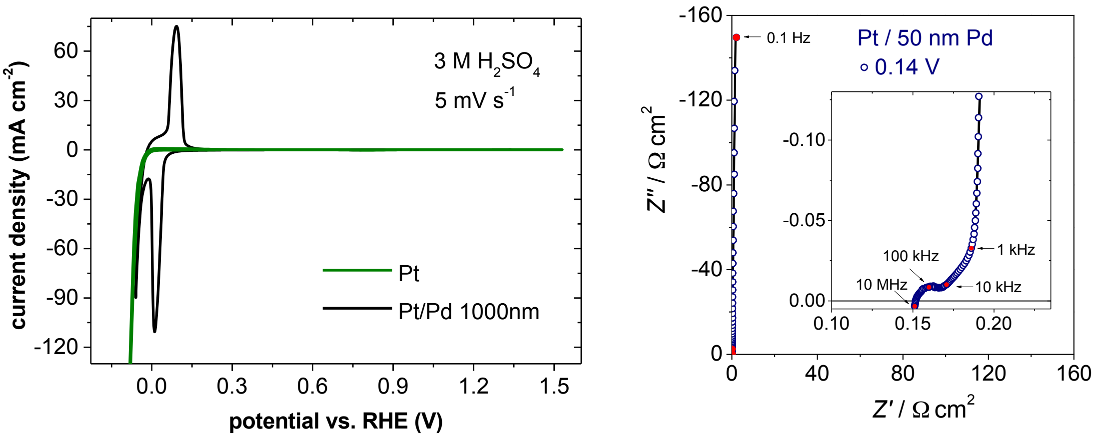

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Effects of Benzenediols on the Oxidative Polymerization of Aniline on Au(111) – Electrochemistry and Scanning Tunneling Microscopy

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This study used cyclic voltammetry (CV) and scanning tunneling microscopy (STM) to address the adsorption and oxidative polymerization of aniline on Au(111) electrode in sulfuric acids containing three isomers of benzenediol (BOH) - hydroquinone (HQ), catechol (CA), and resorcinol (RS).[1]

Molecular-resolution STM images shown in Figure 1 reveal highly ordered aniline adlattices of Au(111) - ($\sqrt{19} \times \sqrt{21}$) at 0.7 V (versus reversible hydrogen electrode) in the presence of 0.1 mM resorcinol, compared with the ($3 \times 2\sqrt{3}$) structure found without BOHs.[2] Three rotational domains of the ordered adlattice are seen in Figure 1a. Molecular resolution STM images shown in Figure 1b and c reveal two spots with different corrugation heights, possibly due to coadsorbed RS and bisulfate anions.

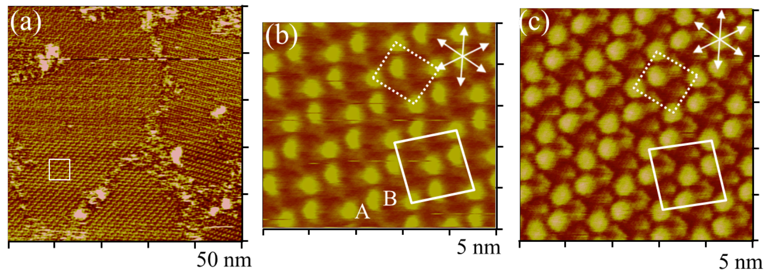

Figure 1. In situ STM images obtained with an Au(111) electrode at 0.7 V in 0.5 M H_2SO_4 + 30 mM aniline + 0.1 mM RS. Panel (a) reveals three rotational domains of the ordered molecular adlayer. Panels (b and c) are the higher resolution STM scans, revealing the molecular structures in the highlighted area using different imaging conditions. The feedback currents and bias voltages were 0.1 nA, -265 mV, and 1 nA, -265 mV for (b) and (c), respectively.

Aniline molecules in the ($\sqrt{19} \times \sqrt{21}$) structure were adsorbed in the zigzagged chains along the <121> direction of Au(111), which caused an anisotropic oxidative polymerization reaction that produced linear polyaniline (PAN) oligomers as seen in Figure 2. The length of PAN molecules depended on the presence of BOHs in the electrolyte, as stated in the figure caption.

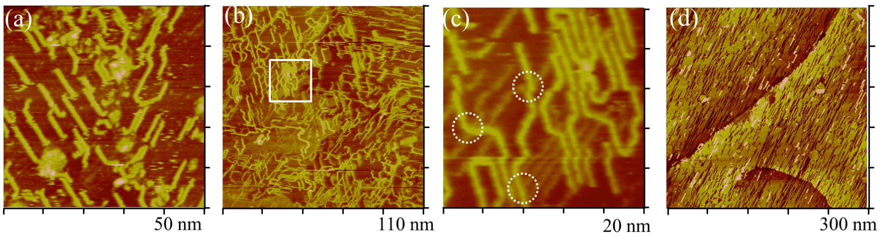

Figure 2. In situ STM images obtained in0.5 M H_2SO_4 + 30 mM aniline + 0.1 mM RS, after the potential was increased from 0.7 to 0.85 V to induce oxidative polymerization of aniline, resulting in linear segments (a) initially, followed by an increase of the molecular length and nucleation of new PAN chains (b). A close-up view of a portion of panel (b) shows crisscrossing of PAN chains between layers, as marked by dotted circles (c). Panel (d) was obtained in electrolyte containing 0.1 mM HQ.

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Development in Methods for Assessing Rebar Corrosion in Complex Ionic Media

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Study of rebar corrosion under the influence of different chloride salts is accompanied by significant complexities. In literature it has been reported that diffusion of chloride ion must be accompanied by the diffusion of cations from the same salt. It has been shown elsewhere that diffusion of cations plays an integral role in the corrosion process. In such an event the reactivity series of metals may be an important factor in the holistic processes. Studies of this category have mostly focussed on rebar corrosion in the vicinity of anions only, discounting the effect of cations. In this regards, a study was undertaken to seek influences of chlorinated salts (NaCl, KCl and $MgCl_2$) on concrete mortar specimens. A normalization approach was used to clearly identify chloride effects in the presence of complex ionic species. Normalizing the data facilitated comparison among the different concentrations of these salts.

Electron Transfer Across an Antifouling Mercapto-hepta(ethylene glycol) Self-Assembled Monolayer

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Claudine Buess-Herman[1]
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Oligo(ethylene glycol) films are known to be very efficient at reducing the non-specific adsorption of biomacromolecules on surfaces, but they often show a tendency to decrease drastically the rate of heterogeneous electron transfer at the modified surface, making them unsuitable for electrochemical biosensing [1]. In this work, the heterogeneous electron transfer across the self-assembled monolayer of a short thiolated oligo(ethylene glycol) is investigated using four redox systems: $[Fe(CN)_6]^{3-/4-}$, $[Ru(NH_3)_6]^{3+/2+}$, $Fc(MeOH)_2^{+/0}$ and $[IrCl_6]^{2-/3-}$.

Fast electron transfer kinetics are evidenced in all cases except the ferri/ferrocyanide couple, for which the electron transfer is completely suppressed. Interfacial characterizations by means of spectroscopic ellipsometry, electrochemical desorption experiments and capacity measurements indicate that the film consists of a fairly hydrated single monolayer with a surface concentration of 4.1×10^{-10} mol cm^{-2}. Size [2], hydrophobicity [3] or charge effects are not sufficient to explain the differences observed between ferri/ferrocyanide and the other redox couples. Instead, the peculiar behavior of $[Fe(CN)_6]^{3-/4-}$ is discussed in terms of the hydration properties of both the monolayer and the electroactive anions.

Even though $[Fe(CN)_6]^{3-/4-}$ is still often presented as an "ideal" one electron reversible system, it is known for a long time to interfacial electrochemists that its heterogeneous electron transfer mechanism is much more complex. This work is yet another illustration of this complexity, and provides new clues on the possible origin of the non-ideality of the electron transfer.

Interestingly, the self-assembled monolayer exhibits the desired antifouling properties against protein adsorption, tested with bovine serum albumin, making this system a promising platform for the development of electrochemical biosensors.

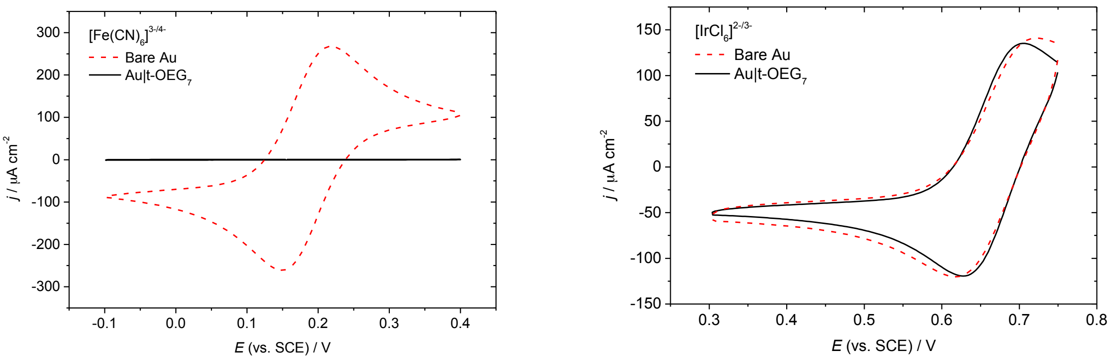

Figure 1. Cyclic voltammograms recorded at 50 mV s−1 at bare gold (dashed red lines) and at mercapto-hepta(ethylene glycol)-coated gold (solid black lines) electrodes, in 0.1 M sodium phosphate buffer, in the presence of $[Fe(CN)_6]^{3-/4-}$ (left) or $[IrCl_6]^{2-}$ (right).

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Electron Transfer Kinetics in Polymetallic carbon-rich Ruthenium(II) bis(σ-arylacetylides) Wires Connected to Gold

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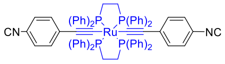
In the field of molecular electronics, Self-Assembled Monolayers (SAMs) of redox-active molecules onto gold surfaces can lead to the formation of integrated materials with significant potential for information storage and transfer.[1,2] Representative examples are metal complexes containing molecular wires connected to surfaces through π-conjugated bridges, exhibiting interesting redox and conductance properties.[3] Incorporation of metal centers into a rigid molecular backbone was shown to improve the charge transport, even for very long wires (up to 40 nm).[4] The easily oxidized metal complexes provide low-lying energy states to the molecular wires, allowing the charge transport processes across the wires to operate through a hopping mechanism which is far more efficient than the tunneling regime for long distance charge transport.[5]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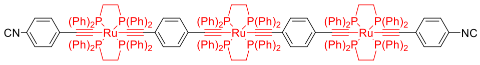
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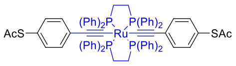
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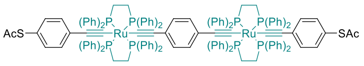
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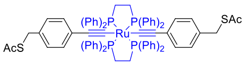
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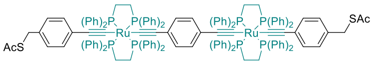
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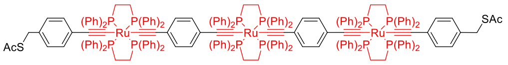
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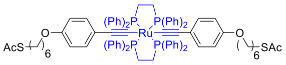
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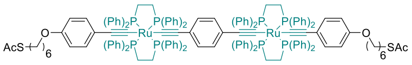
4b

Molecular wires consisting of Ru(II) bis(σ-arylacetylide) organometallics functionalized with different anchoring groups (thiol, isocyanide) connected with different bridges were immobilized onto gold surfaces. The SAMs were studied by wettability, ellipsometric, IRRAS spectroscopic and electrochemical measurements by high speed voltammetry. Similar fast electron transfer dynamics (10^4 s^{-1}) associated with discrete oxidation events (up to 4 distinct oxidation states) at remarkably low potentials (≤ 0.7 V/SCE) were observed for all complexes. Neither the extension of the molecular wires, nor the variation of the anchoring/bridging units influence the electron transfer kinetics. These results highlights the potential of the Ru(II) bis(σ-arylacetylide) complexes as charge-storage medium for processing information in multibit devices at low power consumption

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Highly Selective and Non-Enzymatic Electrocatalytic Detection of Catechol using Flower-like Cu Particles Modified PPy Coated GC Electrode

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Metallized polymers or polymer-metal composites are extensively used as electrocatalysts [1, 2]. Here, the feasibility of Cu-PPy coated GC electrodes (Cu-PPy/GCE) was investigated as electrocatalysts towards catechol oxidation. The Cu-PP/GCE electrodes were prepared by a two step electrodeposition process using chronoamperometry. The polymer was first oxidatively synthesized on the GC electrode at 0.8 V for 30 s from monomer containing solution. Then this electrode was modified with copper particles from metal precursor containing solution at -0.3 V for 15 s. The electrocatalytic and the analytical performances of the Cu-PPy/GCEs were studied using Differential Pulse Voltammetry (DPV), Electrochemical Impedance Spectroscopy (EIS) and Chronoamperometry (CA). Further, the Cu-Ppy modified GC electrodes were characterized using Cyclic Voltammetry (CV), Scanning Electron Microscope (SEM) and FT-IR spectroscopy. The Cu-PPy modified electrodes were found to be highly catalytic and selective towards the detection of catechol. The detection of catechol in tap water samples validated the applicability of our modified electrode for real time applications. SEM image, elctrocatalytic and interference response for the modified electrode in 0.1 M PBS (pH =7) are given in the figure below.

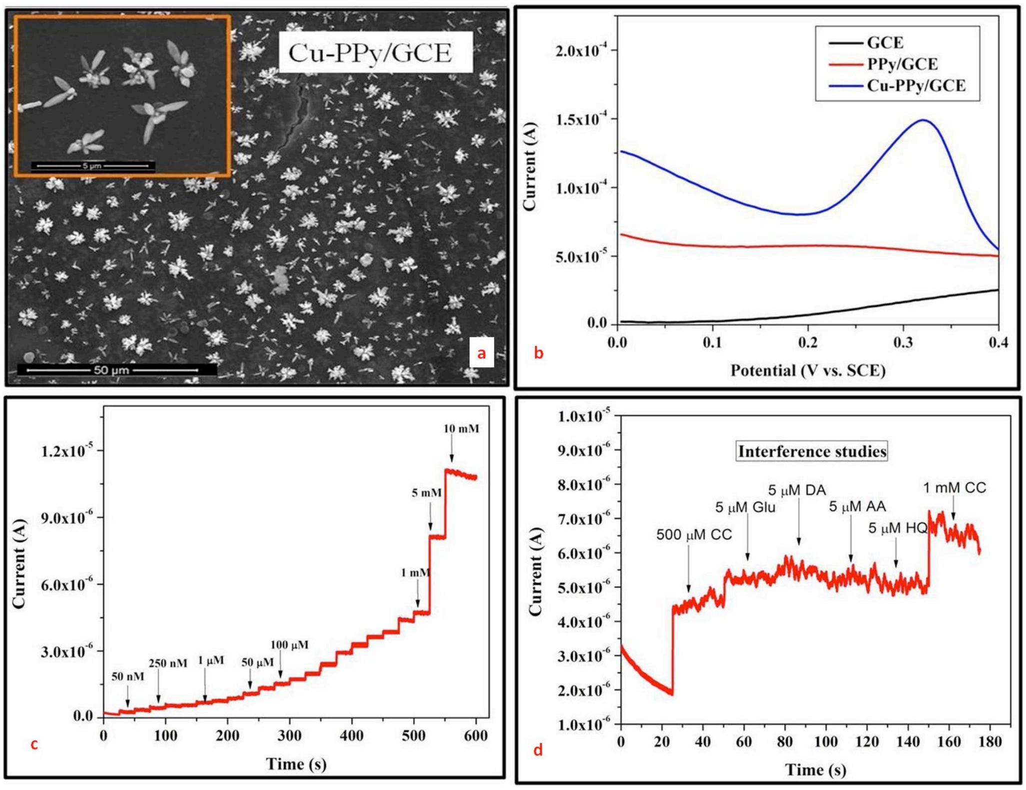

Fig. The (b) DPV, (c) Chronoamperometry and (d) interference response in 0.1 M PBS (pH =7) solution. The SEM image (a) for the Cu-PPy/GCE is also given.

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On the Use of In Situ Electro-Fluorescence Microscopy for the Study of Electrified Bio-Interfaces

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Electrochemical methods are particularly powerful for the study of electrified interfaces, but usually suffer from a lack of spatial resolution (providing typically surface-averaged data). This shortcoming can be efficiently overcome by coupling electrochemical techniques with in situ optical methods such as fluorescence microscopy. An experimental setup combining electrochemical methods and epi-fluorescence microscopy (EC-fluorescence microscopy) is presented, and the potentialities of this setup for the study of electrified biointerfaces are illustrated.

Self-assembled monolayers of two biomolecules have been investigated with our original setup [1]. A thiolated DNA probe, labelled with a fluorescent BODIPY moiety, is immobilized onto gold electrodes, together with a mercaptobutanol diluent, using various procedures (one step co-adsorption versus two steps sequential assembly, concentration ratios…). While capacity curves are rather insensitive to the way of preparation of the mixed monolayer, fluorescence images reveal significant differences. Reductive desorption experiments were conducted within the EC-fluorescence cell, showing a complete desorption in the first potential sweep. Both capacity and fluorescence curves indicate a two stage desorption. Resorting to Au(111) and Au(210) single-crystals, it is demonstrated that these two stages are connected with the substrate crystallography.

The results obtained on a second system, consisting of a self-assembled monolayer of a peptide fragment of the p53 protein labelled with a fluorescein fluorophore are presented.

For both systems, the coupling of electrochemistry and fluorescence microscopy provides insightful information regarding the spatial heterogeneity of the biointerfaces.

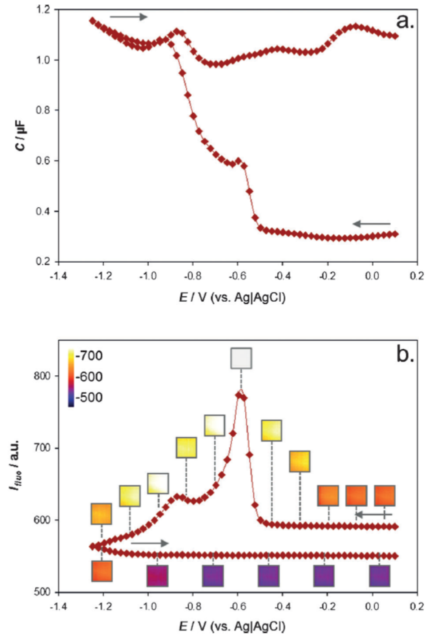

Figure 1. Representative capacitance–potential (a) and fluorescence–potential (b) curves recorded in 10 mm phosphate buffer at a DNA mixed SAM-modified polycrystalline gold electrode.

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Reductive Grafting of In Situ Produced Diazonium Cations in a BrØnstedt Acidic Ionic Liquid – Evidence of an Efficient Self-Limiting and Self-Patching Film Growth

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Joëlle Rault-Berthelot[a]
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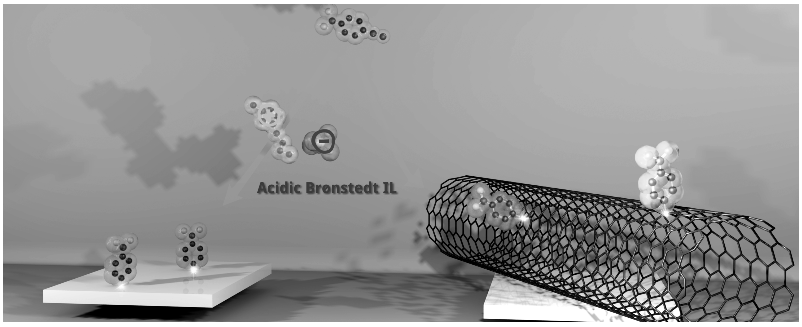
Imidazolium-based Brønstedt acidic ionic liquid, 1-butyl-3-methylimidazolium hydrogensulfate, [BMIm][HSO$_4$] was used as electrolyte for the grafting of glassy carbon/PPF (pyrolyzed photoresist films) electrodes and carbon nanotubes from nitrobenzene diazonium cations.[1] The diazonium cations were simply produced *in situ* in the acidic ionic liquid containing 4-nitroaniline and NaNO$_2$. The electrochemical and atomic force microscopy (AFM) studies of the electrografted solid electrodes reveal that a particularly interesting self-limiting and self-patching process occurs in the highly viscous ionic liquid. Thinner and denser films were obtained in the ionic liquid, as compared with films formed in acidic aqueous HCl solution.

Due to the dispersion properties of imidazolium-based ionic liquids towards carbon nanotubes, the described grafting method could have been further extended to single- and multi-walled carbon nanotubes,[2] following either an electrochemical or a chemical route. This simple and soft method allows i) the facile electrochemical functionalization of carbon nanotubes from the nitrobenzene diazonium cations *in situ* produced in [BMIm][HSO$_4$] and ii) the facile electrochemical characterizations of the functionalized carbon nanotubes materials.[3]



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Aqueous electrochemistry of magnesium

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The aqueous electrochemistry of magnesium has provided significant frustration to those researching the corrosion of magnesium or primary magnesium batteries. The relatively unique electrochemical behaviour of magnesium is presented, employing a number of methodologies. It is shown that magnesium electrochemistry is influenced by significant ‘cathodic activation’. This cathodic activation was studied in a range of conditions revealing several key characteristics, including pH dependence, and composition dependence. Cathodic activation implies an enhanced ability to support water reduction (i.e. the cathodic reaction) on surfaces that have undergone anodic exposure or some dissolution. This activation leads to superfluous hydrogen, which is then also a key contributor to the so-called ‘negative difference effect’, persistent hydrogen evolution, and parasitic discharge. A number of experiments are combined in order to provide a holistic description of the cathodic activation effect, and its physical origins – which is of key significance to understanding electrochemistry of reactive metals (not just magnesium).

CO_2 Capture and Electrochemical Conversion using Ionic Liquid [BMIM][TF_2N]

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The electrochemical reduction of CO_2 into $HCOO^-$ and other hydrocarbons on platinum and glassy carbon are well described in the literature. This work aims to develop and characterize platinum and glassy carbon as a cathode material and describe a suitable ionic liquid supporting electrolyte for CO_2 solvation. The catholyte to be explored is [BMIM][TF_2N] while the anolyte will remain as KOH. The reactor is batch type with separation of the catholyte and anolyte achieved using a Nafion membrane.CO_2 gas will be bubbled into the catholyte and reduced at the platinum and glassy carbon cathode. Various parameters will be investigated. Results for both platinum and glassy carbon will be analyzed and compared. Acquired data will be used to elucidate the efficiency of the platinum cathode and glassy carbon cathode in the reduction of CO_2. At completion, this work is able to describe the optimal conditions for electrochemical reduction of CO_2 into $HCOO^-$ and hydrocarbons within the scope of study.

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Electron Transfer through 3D Monolayers on Au_{25} Clusters

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Monolayer-protected gold clusters (MPCs) are systems in which a molecular layer of suitable ligands, usually thiolates, stabilizes and protects an otherwise reactive gold core. As the number of gold atoms decreases, MPCs start displaying a borderline behavior between that of actual molecules and larger nanoparticles. These protecting monolayers are often represented as the 3D equivalent of 2D self-assembled monolayers (SAMs) on extended gold surfaces. However, despite the growing relevance of MPCs in important applied areas, such as catalysis, sensors and nanomedicine, our knowledge of the dynamic structure of these 3D SAMs is quite limited. This is particularly true for the ultrasmall nanoclusters displaying molecular properties (gold cores of diameter <1.6 nm). $Au_{25}(SR)_{18}$ (core = 1 nm) is a stable thiolate-protected gold nanocluster that has provided and still provides the true "gold mine" for gaining insights into the properties[1-4] and potential applications of molecular MPCs, as well as developing and testing new concepts at the nanoscale.

We prepared a large series of monodisperse $Au_{25}(SC_nH_{2n+1})_{18}$ clusters (with n varying between 2 and 18; linear but also branched chains) and studied how electrons tunnel through the corresponding monolayers. Heterogeneous electron-transfer results, nicely supported by ^1H NMR spectroscopy and molecular dynamics calculations, provided an interesting, self-consistent picture of how an ultrasmall gold core talks with the environment through/with its protecting but not-so-shielding monolayer. The distance dependence of the electron-transfer rate in solution was then compared with that of electron transfer in the solid state, as obtained by drop casting the same Au_{25} nanoclusters onto interdigitated electrodes. These and further results concur in showing that electrochemically determined electron-transfer rates provide the most efficient and sensitive tool for probing the solution-phase structure of the otherwise elusive 3D monolayers of molecule-like MPCs.

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Development Of Sensitive Voltammetric Progesterone Sensor Using Micro-Rod Tin Modified Glassy Carbon Electrode In The Presence Of Cetyltrimethylammonium Bromide Surfactant

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A sensitive Progesterone (P4) sensor based on tin microcrystal modified glassy carbon electrode in the presence of Cetyltrimethylammonium Bromide surfactant has been explored. The potentiostatic electrodeposition of micro-rod shaped Sn particles has obtained at applied lower overpotential with 120s of deposition time in an acid chloride electrolyte solution and characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and energy dispersive X-ray spectroscopy (EDS). The electrochemical behavior of P4 has been discussed in different electrolytes such as phosphate buffer (PB), Britton-Robinson (BR) and sodium hydroxide (NaOH) solutions. The effects of various surfactants such as Sodium Dodecyl Sulfate (SDS), Cetyltrimethylammonium Bromide (CTAB), and TritonX-100 (TX-100) on the reduction of progesterone were studied by cyclic voltammetry. The tin-modified GC electrode exhibits a facile electrocatalytic response with respect to decrease in overpotential for the reduction of P4 in the presence of cationic surfactant CTAB. Moreover the influence of concentration, scan rate and pH were studied. Analytical sensing of the biological hormone progesterone has been carried out through Differential Pulse Voltammetry, Amperometry and Electrochemical Impedance Spectroscopy methods. It shows an enhanced sensitivity, wide linear range of 2 – 80 μM and lower limit of detection (LOD) of 0.1 μM (S/N=3). Moreover, the proposed electrode exhibit good reproducibility (RSD < 5%) and stability with minimal interference from the coexisting electroactive compounds such as ascorbic acid, dopamine and uric acid.

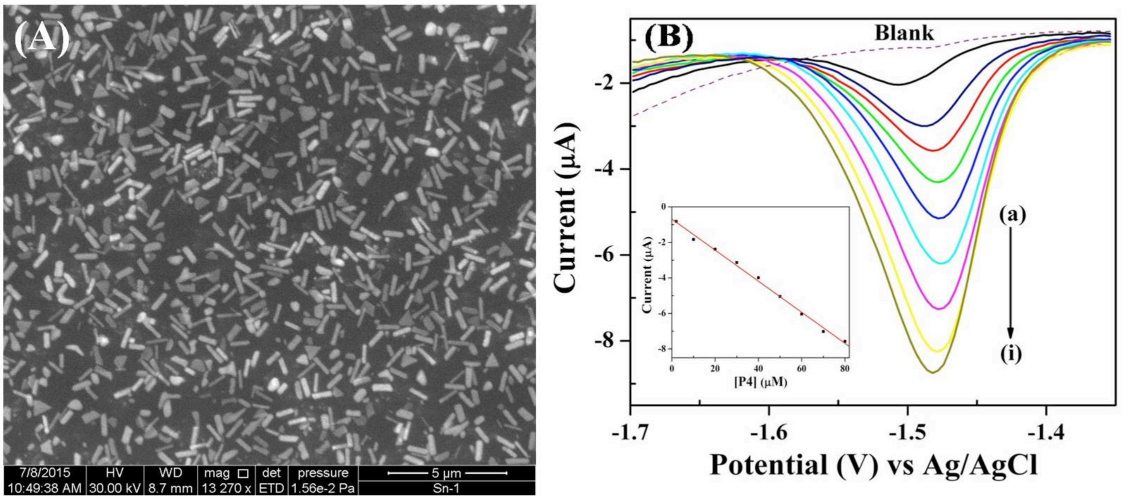

Fig. 1 (A) Scanning Electron Microscopy (SEM) image of electrodeposited Sn on GC electrode and (B) Differential Pulse Voltammograms (DPV) in 0.2 M NaOH solutions for various concentrations of progesterone. The inset depicts the calibration plot ranging from 2 to 80 μM.

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Enhanced high temperature performance of $LiFe_{0.5}Mn_{0.5}PO_4/C$ cathode materials via surface modification

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Abstract

This work reported a ball-milled solid-state method to prepare $LiFe_{0.5}Mn_{0.5}PO_4/C$ (LFMP/C) composite materials by using LiH_2PO_4、MnO_2、Fe_2O_3、citric acid ($C_6H_8O_7$) and sucrose ($C_{12}H_{22}O_{11}$). The citric acid was used as a complex agent and sucrose was used as a carbon source. The $Li_4Ti_5O_{12}$ (LTO)-surface modified on LFMP/C was carried out by a sol-gel method. The composite materials was sintered at 600-750°C in an Ar atmosphere for 10-15 h. It was found that the optimum temperature was at 650°C. The chacterististic properties of the pristine and surface-modified LFMP/C composite cathode materials were examined by micro-Raman spectroscopy, XRD, SEM/EDX, TEM, EA and AC impedance method. The 2032 coin half-cell was used to investigate the electrochemical performance at various rates. It was found that the specific discharge capacities of 1%LTO-coated $LiFe_{0.5}Mn_{0.5}PO_4/C$ composite cathode materials achieved ca. 161.18, 154.71, 148.82, and 120 mAh g^{-1} at 0.1, 0.2C, 1, and 10C rate, respectively. In particular, they also showed very high current efficiency, ca. 98-99%. The cycle-life test also revealed excellent charge/discharge stability (CR%=98%) at 1C/1C rate for 300 cycles without obvious capacity fading. Apparently, the LTO-surface modified $LiFe_{0.5}Mn_{0.5}PO_4/C$ composite material can be a good candidate for high temperature Li-ion battery applications.

Keywords: $LiFe_{0.5}Mn_{0.5}PO_4$, Fe_2O_3, $Li_4Ti_5O_{12}$ (LTO) surface-modified, Cathode materials, A sol-gel method

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Feasibility of Overoxidized Polyaniline towards Anion Exclusion Behavior and Sensing Applications

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Combination of metal like conductivity and polymeric properties e.g. flexibility, low density, ease of structural modification etc render conducting polymers as a potential candidate in a wide range of applications viz. sensor devices, Supercapacitors, electro-catalysis, electrochromism batteries etc [1-3]. Among various conducting polymers, Polypyrrole (PPy) and polyaniline (PANI) have attracted a special interest due to its higher electrical conductivity (which can be tuned from 10^{-4} Scm^{-1} to 10^{3} Scm^{-1}), appreciably environmental stability and good mechanical properties. Overoxidized conducting polymers have not received much attention in these aspects. Although overoxidized form of PPy and the substituted PPy were employed to some extent in the aforementioned applications [4], but the utilization of overoxidized PANI is rare in this context. In the present investigation, the feasibility of overoxidized PANI (oPANI) is demonstrated towards the sensing of pH and ascorbic acid (AA). oPANI has been prepared by anodic sweeping (potentiodynamic cycling) of the electrodeposited PANI on GC electrode in 0.1 M KCl solution. However the electrodeposition of PANI is carried out on the GC electrode by potentiostatic polymerization in 0.1 M SDS solution. The characterizations of PANI and its overoxidized form have been carried out by using SEM and UV-Vis studies. Besides, the overoxidation process leads to the change in color of PANI from green to pale brown. oPANI possesses the anion exclusion behavior wherein the overoxidation process leads to the inducement of anionic characters by incorporating the counter ions into the polymer matrix. Further, the sensing ability of oPANI towards H^+ ions as well as AA has been studied.

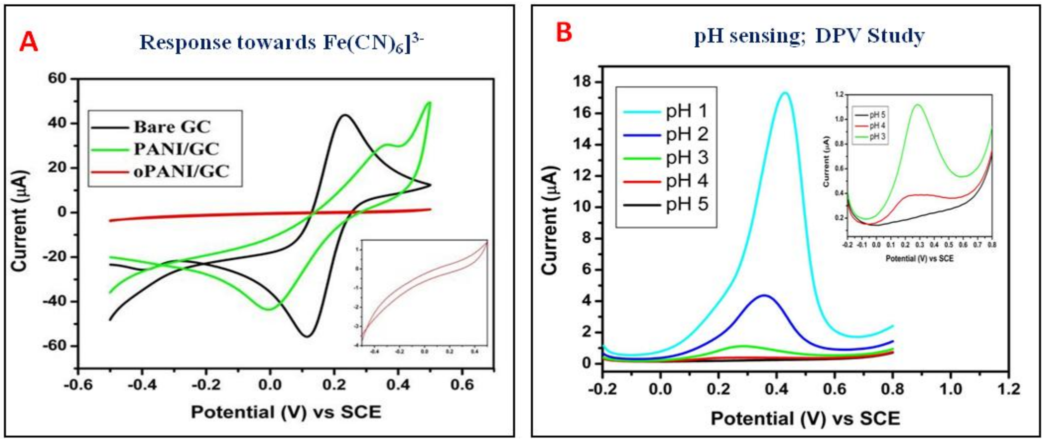

Fig. 1(A) Cyclic voltammetric (CV) response of oPANI/GC exhibiting the anion exclusion behavior wherein $[Fe(CN)_6]^{3-}$ is used as anionic redox probe. Inset represents the featureless voltammogram of oPANI towards $[Fe(CN)_6]^{3-}$. (B) Differential pulse voltammograms depict the feasibility of oPANI/GC electrode towards pH sensing. Inset represents the DPV response at different pH which is not clear in Figure.

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Vanadium Electron Transfer on Modified Carbon Electrodes

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The Vanadium Redox Flow Battery (VRB), invented and developed by Maria Skyllas-Kazakos and her co-workers at the University of New South Wales, represents one of the possible options for efficient electrochemical energy storage [1]. One of the contemporary challenges of VRBs is their low power density and therefore catalysis of the redox reactions is desirable [2].
However, currently in the literature there is not even consensus which of the two half-cell reactions, the V^{2+}/V^{3+} or the VO^{2+}/VO_2^+ redox reaction, is faster. Similarly, reports contradict each other regarding the influence of carbon surface functional groups. Some paper assign catalytic activity for one or both half-cell reactions to carbon surface functional groups, others do not.

We will show that this uncertainty in the literature is due to two factors:

- An apparent catalytic effect appears when porous electrode materials are investigated with linear or cyclic voltammetry. The porosity reduces the separation between anodic and cathodic peak suggesting enhanced kinetics when indeed only an interplay of enlarged electrochemical surface area and impeded diffusion within the porous electrode is present [3];
- The faradaic current is proportional to both the electrochemical active surface area A^{ECSA} and the electron transfer constant k_0: $I \;\square\; \boldsymbol{A^{ECSA}}\ \boldsymbol{\kappa_o}$. As both parameters vary with change in electrode composition, it is often difficult to distinguish catalytic from surface-area effects.

We have recently presented a method that allows to monitor changes in A^{ECSA} and k_0 while varying the concentration of surface functional groups on carbon electrodes [4]. The experimental procedure relies on electrochemical impedance spectroscopy, which yields an observable for A^{ECSA}, the double layer capacitance C_{DL}, and an observable for both A^{ECSA} and k_0, the charge transfer resistance R_{CT}. Combining C_{DL} and R_{CT}, the contribution from A^{ECSA} can be eliminated and only the effect of k_0 remains.

This method was employed to investigate the kinetics of the V^{2+}/V^{3+}, Fe^{2+}/Fe^{3+} and VO^{2+}/VO_2^+ redox reactions on multi-walled carbon nanotubes [4] and commercial graphite felt electrodes [5]. The surface chemistry of the carbon electrodes was modified by chemical and thermal treatments and monitored by SEM, XPS, FTIR, TGA-MS and Raman spectroscopy.

We will show unambiguously that surface functional groups on carbon enhance the kinetics of the V^{2+}/V^{3+} and Fe^{2+}/Fe^{3+} redox reactions, but impede the VO^{2+}/VO_2^+ redox reaction.
We will present possible reaction mechanisms that explain this diametrical behavior and discuss consequences for the VRB.

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Hofmeister Effects on Glucose oxidase-Redox Hydrogel Electrode

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Redox hydrogel, structured with redox mediator-bound polymer and redox enzyme by electrostatic interaction and/or crosslinking, is one of the promising technique to immobilize enzyme and mediator on an electrode surface [1]. Hydrogel-modified electrode provides high and stable glucose oxidation catalytic current because the enzyme and mediator are packed in high concentrations. It has been reported that the reversible change of the catalytic glucose-oxidation current by NaCl; the current decrease in the presence of NaCl in the solution, and the recovery by removing NaCl. This phenomena is attributed to that NaCl countered electrostatic attraction between enzyme and redox polymer and repulsion in cationic polymer. The effect of nature and concentration of the electrolyte to the faradaic properties of an enzymatic electrode reaction should be considered for designing the efficient hydrogel-electrode.

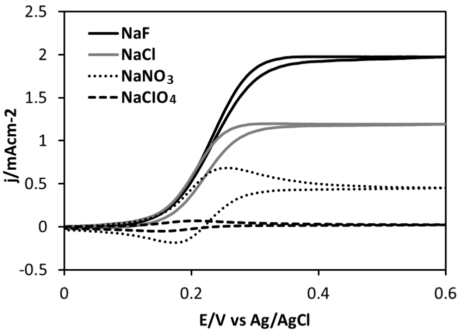

Fig. 1. CVs for glucose oxidation current; total hydrogel loading of 600 μg·cm−2, each solution containing 0.5 M sodium salt and 0.2 M of glucose, 0.1 M of phosphate buffer, pH 7.0, 25 °C, 2000 rpm, 20 mV·s−1.

In this study, hydrogel-modified electrode was prepared by drop-casting biocatalyst solution containing glucose oxidase, poly(1-vinylimidazole) complexed with [Os(bipyridine)$_2$Cl] and poly(ethylene glycol) diglycidyl ether on a glassy carbon electrode and dried at 4 °C for 18 h. Figure 1 shows cyclic voltammograms of glucose oxidation current in 0.1 M phosphate buffer solution in the absence and presence of 0.5M of NaF, NaCl, $NaNO_3$, $NaClO_4$. The magnitude of steady-state current depend on the nature of the electrolyte used; the current response decreased with increasing the hydrophobicity (chaotropicity) of the anion. The kosmotropic/chaotropic property of anions affects the deswelling/swelling of the hydrogel structure and the interaction between the enzyme and Os complex. The effect of cation on the current response was weaker than that seen with anions.

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Effects of Aluminum Surface Properties on the Cycleability of Al-ion Battery

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Aluminum metal, which is less reactive, abundant and cost effective, has been suggested as an electrode material for energy conversion device. Transport of trivalent Al^{+3} during charging and discharging processes offers a competitive alternative to single electron Li-ion battery. However, aluminum anode surface can be covered with passive aluminum hydroxides and hydrogen gas can be evolved on the anode surface in aqueous system. Those phenomena limit the development of rechargeable aluminum battery and require a battery system of nonaqueous-based electrolyte. Recently, $AlCl_3$ with 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) was suggested as an electrolyte for a rechargeable Al battery. (1,2) When the molar ratio of $AlCl_3$/([EMIm]Cl is greater than 1 (Lewis acid), Al dissolution and deposition reactions are $Al + 7AlCl_4^- = 4Al_2Cl_7^- + 3e$ during cycling. Furthermore, the formation of dense Al at less than 100 mA/cm^2 of deposition reaction suggests the possible rapid charging reaction, when there is no limitation in anodic reaction during charging.(3) However, Al dissolution reaction is not well-discussed in $AlCl_3$/([EMIm]Cl electrolyte. Aluminum metal is naturally covered with air-formed oxide film, which works as a protective layer. When the Al metal is exposed to chloride-containing solution, surface oxide film is locally attacked and anodic dissolution of aluminum is followed. Presence of oxide film determines the reactivity of aluminum metal and the role of surface oxide films in $AlCl_3$/([EMIm]Cl electrolyte needs to be elucidated to develop a rechargeable Al-ion battery system.

In this work, both *as-is* and electropolished aluminum electrode were prepared and the dissolution behaviors of aluminum with immersion time and electrolyte compositions were investigated with surface morphology studies (SEM) and electrochemical methods (cyclic voltammetry, electrochemical impedance spectroscopy). Additionally, surface area of aluminum was magnified with electrochemical etching and it was applied as an anode for the rechargeable Al-ion battery. Effects of various oxides and carbon cathode materials on the cycleability and capacity of battery system were investigated.

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Simultaneous Impedance Spectroscopy and Optical Microscopy to Investigate Cells Attachment and Spreading

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In a normal environment, cells are responding to the signals coming from their external environment, and the way they react often determines their fate. These signals can come from multiple soluble chemicals (soluble cues) such as secreted proteins from neighboring cells. These cues usually trigger incredibly complicated pathway of events inside the cells, which lead to certain cellular responses. The mechanisms behind the responses are even more sophisticated as physical property of surrounding environment (adhesive cues) such as ligands in the extracellular matrix (ECM) have also their own effect on the signaling pathways and the overall cells responses. Specifically, the Arg-Gly-Asp ligands present in ECM have been mainly known for determining the extent of the cells attachment and spreading in its environment through binding to cellular integrins. It is crucial to achieve a better understanding of the possible links between signaling networks provoked by soluble and adhesive cues.

We have coupled fluorescence microscopy and electrochemical Impedance spectroscopy simultaneously to provide more comprehensive information about this connection. To model the adhesive cues, the interdigitated Indium−tin oxide (ITO) surfaces were modified to present different RGD densities. Fluorescence microscopy was used to monitor the activity of G-protein coupled receptors (GPCR) by measuring the intracellular calcium flow, while the impedance spectroscopy was used to track the minute morphological changes all in response to histamine, as an example of soluble cues, addition on the modified ITO surfaces. The ITO surfaces with different RGD ligand spacing were prepared by modifying the surfaces with different ratios of hydroxyl-terminated and methoxy-terminated 1-aminohexa(ethylene oxide), followed by incubation in 20 μg/ml RGD solution on a cell-inert background, which was developed on the surface previously. The cell-surface interaction was investigated by seeding 10^4 HeLa cells/ cm^2 on surfaces for 3 h, following by fixing, and staining with phalloidine-Alexa 488 to determine the extent of cells spreading. For impedance spectroscopy, the resistance of the cell layer was measured at 40 kHz, since plating the cells, while the calcium flow in response to the addition of histamine was measured using fluorescence microscopy after loading the cells with Fura-2 AM calcium dye. A custom-made chamber from Micrux (Oviedo, Spain) was used to run the simultaneous experiment. The fixed cell-surface study showed that the cells morphology and spreading is highly dependent to the amount of RGD ligands present on surfaces. The microscopy results indicate that histamine-mediated GPCRs activity can significantly induce the flow of calcium in the cytosol. In contrast, the impedance spectroscopy showed that altering the ECM-cell integrin interaction by introducing different RGD ligands to the surface modulates the cells morphology on the surface. More importantly, we observed that the presence of different RGD ligands on the surfaces dramatically changed the amount of released calcium. Figure 1 shows the change in impedance and calcium ion release in response to histamine on surface modified with $1{:}10^3$ of hydroxyl-terminated and methoxy-terminated 1-aminohexa(ethylene oxide) as an example. This surface was demonstrating the highest amount of released intracellular calcium while it showed the lowest increase in the amount of impedance among the surfaces that were used in this experiment.

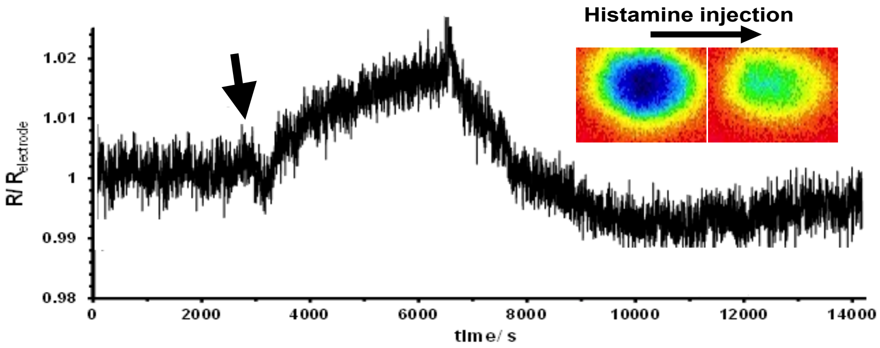

Figure 1. The relative increase in impedance value in response to 100 μM histamine on ITO surfaces modified with 1:1000 ratio of 1-aminohexa(ethylene oxide) to 1- aminohexa(ethylene oxide) monomethyl ether. The image is an example of the fluorescence images showing the increase in calcium flow in response to histamine, where blow-red refers to low-high.

Polymer Gelification of an Ionic Liquid for Electrochemical Gas Sensing

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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 (O_2) 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-methylimida-zolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$), 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 % m_{PMMA}/m_{Tot}. 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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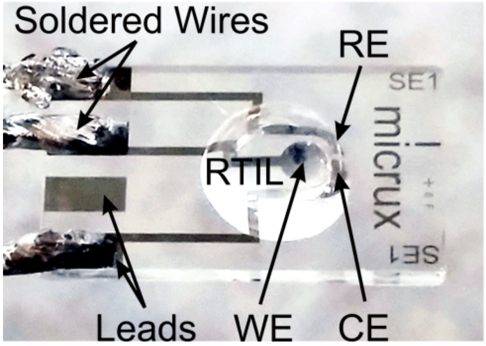

Fig. 1 Photo of a Pt-TFE (purchased from Micrux) with a layer of GPE deposited over the electrodes.

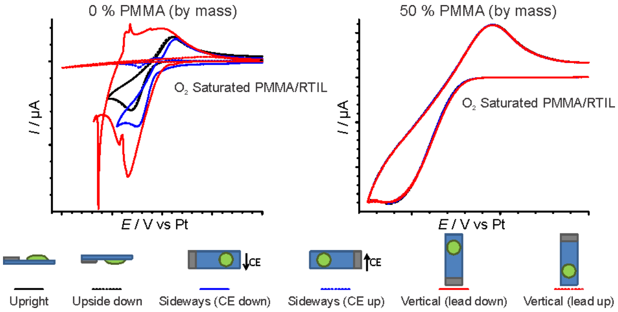

Fig. 2 CVs of $O_2/O_2^{\bullet -}$ redox couple in the neat $[C_2mim][NTf_2]$ and the 50% PMMA doped $[C_2mim][NTf_2]$, with the Pt-TFE positioned in different orientations.

Electrochemical Response of Redox Dendrimers as surface modifiers and redox probes in SECM experiments.

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Redox dendrimers represent a large class of molecular objects with numerous possibilities to obtain a desired function by the adaptation of their topology and the possibility of introducing specific redox-active metal centers. Among them, ferrocenyl terminated dendrimers are interesting objects for electrochemical investigations as they display fast and reversible charge transfer with an electrode and they often exhibit properties that are not the simple addition of individual redox groups. [1]

Two different strategies, based on the electro-reduction of aryl diazonium salts, were developed in our group to immobilize redox dendrimers onto carbon surfaces. The first strategy consists on the electro-grafting of an insulating polyarylcarboxylate films followed by strong adsorption of the redox dendrimers by electrostatic interaction on the organic layer. This fast and efficient strategy allows us to study the basic electrochemical properties of such modified interfaces by Cyclic Voltammetry (CV) and Scanning Electrochemical Microscopy (SECM) showing efficient and fast electrochemical communication between the redox centers. [2] Due to stability problems for advanced applications, we develop a second strategy were dendrimers are covalently bonded to the carbon substrate. It consist first on the electro-grafting of an ethynylphenyl monolayers followed by immobilization of dendrimers backbone by click chemistry reaction between the modified surface and azido-terminated dendrimers. Introduction of redox functionalities was performed in a second time by coupling the free azido termini of the immobilized dendrimers with ethtynylferrocene. SECM experiments were performed on such modified interfaces which shown to exhibits specific sensing properties thanks to the dendrimeric nature of the interfaces. [3]

Finally, as redox dendrimers display many interesting properties, we studied their efficiency as redox mediator in SECM experiments, to probe surfaces modified by insulating layers. These first experiments reveal that charge transfer are considerably enhanced when the charges are transferred by the redox dendrimers instead of a single redox molecule. [4]

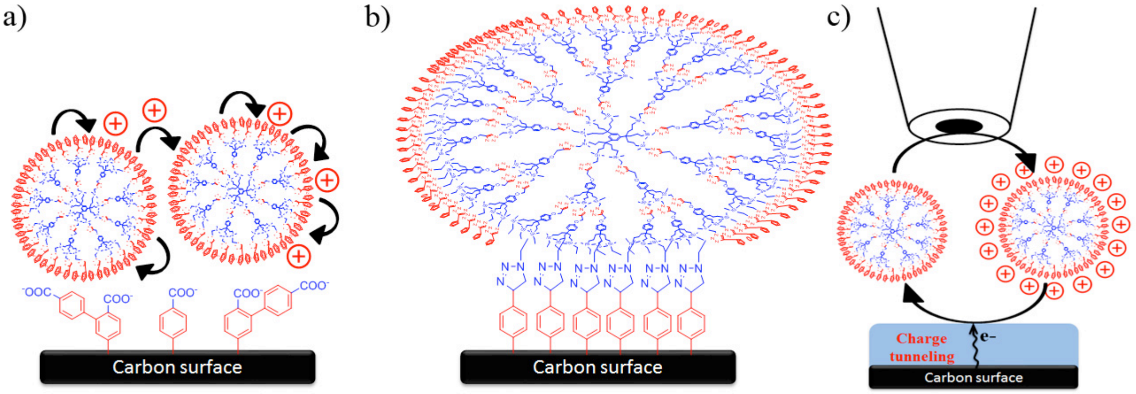

Figure 1. Representative schemes of redox dendrimers immobilized by a) electrostatic interactions and b) click chemistry coupling reaction. c) Use of redox dendrimers as redox mediators in SECM experiments.

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Electro-adsorption of Porphyrin Films at Polarised Soft Interfaces

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Common to all **solar energy conversion devices** are the abilities to harvest light and then separate the products of the photo-reaction, minimising recombination.[1] Typically charge separation takes place at the surface of nanostructured electrodes, often covered with photosensitiser (PS) molecules such as in dye-sensitised solar cells (DSSCs). However, the use of solid state architectures made from inorganic materials leads to high processing costs, occasionally the use of toxic materials and an inability to generate a large and significant source of energy due to manufacturing limitations.[2] Certain soft interfaces formed between aqueous and organic electrolyte solutions of low miscibility (*e.g.,* trifluorotoluene) are electrochemically active in that it is possible to precisely control the Galvani potential difference ($\Delta^{w}_{o}\phi$) between the two adjacent liquids (*i.e.,* to "polarise" or electrify the interface), and thus drive charge transfer reactions.[3] Here we present our most recent finding **exploring a new paradigm in solar energy conversion by achieving efficient charge separation at electrochemically active soft interfaces, without solid electrodes** (Figure 1), by modifying the soft interfaces with films of dyes, *i.e.,* porphyrins.

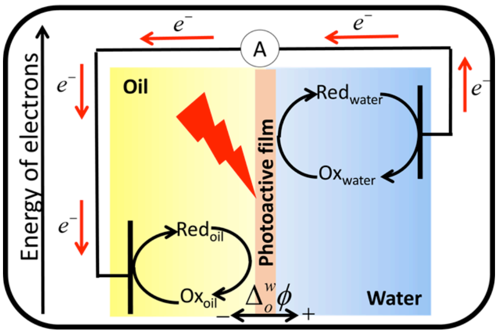

Figure 1: Scheme illustrating the concept that photoactive films trap solar energy, generating high-energy electrons. In theory this allows electron transfer across the interface between redox couples that thermodynamically are incapable of heterogeneous electron transfer in the dark due to their respective redox potentials in each phase.

Generated photocurrents at soft interfaces are directly proportional to the interfacial surface concentration of ground state PSs present at the interface. PSs present in the bulk aqueous or oil phase are not involved in electron transfer with species in the adjacent phase.[4] All previous studies relied on electrostatically increasing the interfacial surface concentration of ground state PSs by polarising the soft interface positively or negatively,[4] or by creating "neutral dimers" through formation of ion-association complexes between cationic and anionic PSs, respectively, in the aqueous phase.[5] The latter are not electrostatically repelled by the organic electrolyte anions and cations and, thus, adsorb at the interface more strongly than either monomer.[5] Importantly, we have found that *all previous studies with zinc porphyrin PSs at soft interfaces were carried out under sub-optimal conditions, severely limiting photoconversion efficiencies.* Utilising liquid-liquid electrochemistry, we electro-adsorbed a photoactive film of zinc tetrakis(4-carboxyphenyl)porphyrin (ZnTPPc) at water | trifluorotoluene interfaces by judicious optimization of the experimental conditions, producing an order of magnitude increase in the photocurrents in comparison to the previous state-of-the-art.

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Photocatalytic activity of Ag-TiO_2-graphene ternary nanocomposites

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Ag-TiO_2-graphene ternary nanocomposites were fabricated by a photocatalytic redox method using Ag, P25 (TiO_2) and graphite oxide as source materials. The optimum weight ratio of graphene in the ternary nanocomposites was explored to achieve higher photocatalytic activity. The characteristics of the nanocomposites have been examined by X-ray diffraction, X-ray photoelectron, UV-Vis absorption and Raman spectroscopies, respectively. Their morphologies and microstructures were obtained by scanning and high-resolution transmission electron microscopies. It was observed that TiO_2 and Ag nanoparticles were located/dispersed on the graphene nanosheets. By electrochemical impedance spectroscopic (EIS) and cyclic voltammetric (CV) analyses, it was evidenced that a higher graphene content led to better conductivity as well as a rapider charge transport rate. The results have showed that a higher content of graphene would contribute to photodegradation efficiency. The improved photocatalytic performance can be attributed to enhanced absorption in the visible region and excellent electron mobility of graphene. This work has demonstrated that the Ag-TiO_2-graphene nanocomposite containing an appropriate weight ratio of graphene (5:1) is a promising photocatalyst for both organics decomposition and water splitting.

Biosynthesis of iron particles using *Camellia sinensis* extract

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The interest in nanotechnology in environmental remediation has been increasing recent times. Metallic nanoparticles of different sizes and morphologies can be readily synthesized using chemical and physical methods.(1-2) However, these techniques involve hazardous chemicals as organic solvents, reducing agents and nonbiodegradable products.(3) They are potentially harmful to the environment and biological systems. The biosynthesis of nanoparticles has been suggested in environmental friendly alternative to chemical and physical methods. (4-5) Nanomaterials have been synthesized using microorganisms (6) and plant extracts. (7) The aim of the study was biosynthesis of green iron nanoparticles (GnIP) using extraction of natural products or wastes. In this study, GnIP synthesis with green tea (*Camellia sinensis)* leaf extract was investigated to use water and wastewater treatment.15 g leaf was extracted in water at 80 °C during 15 minutes before adding 0.1 M $FeCI_3.6H_2O$ as a source of iron. Zetasizer (Malvern 500210) size distribution results and SEM (EVO 40) images showed the formation of GnIPs size ranging from 10-100 nm. This study indicated GnIPs can be formed successfully with green tea leaf extract without any hazardous chemicals and they can be used effectively in a variety of water and wastewater treatment method.

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Heavy Metal Quantification at Bismuth Electrodes in Biomass-Dissolving Electrolytes – Significant Cation Effect Upon the Interface

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Bismuth is recognised as an excellent material for the anodic stripping voltammetric (ASV) quantification of some heavy metals (dissolved in an electrolyte), and a 'greener' alternative to mercury.[1] Ionic liquids are 'pure' electrolytes, which are also unrivaled solvents for complex systems such as biomass,[2] *e.g.* they can be used to fully dissolve wood, nut shells, algae, through to even food items such as chilli, under facile and safe conditions compared to typical digestions.[3] Certain aqueous hydroxides with large, bulky quaternary ammonium cations have been known since the 1930's to rapidly dissolve complex matrixes such as cellulose and rice husks.[4]

This study has investigated combining anodic stripping voltammetric quantification of heavy metal with facile digestion electrolytes such as ionic liquids and aqueous hydroxides. Discussion will primarily focus upon the case of cocoa powder and tetraalkylammonium hydroxides.

The World Health Organisation recommends cadmium contents of cocoa powders should not exceed 0.3 mg/kg; four cocoa powders were purchased from an Australian supermarket and were found to have cadmium contents between 0.1 and 1.0 mg/kg. While the cocoa powder did not dissolve in nitric acid or water, it was partially soluble in 1.5 M sodium hydroxide and 1.5 M tetramethylammonium hydroxide, and fully soluble in 1.5 M tetraethylammonium and tetrabutylammonium hydroxide.

Attempts were made to quantify cadmium in these facile digestion electrolytes using a bismuth working electrode to pre-concentrate the cadmium metal. When negative potentials are applied, the tetrabutylammonium system was found to form a dense double layer at the bismuth electrode surface, such that cadmium reduction and alloy formation (amalgamation) cannot even occur. Cadmium reduction is partially suppressed in the presence of tetraethylammonium cations; cadmium insertion and remove from the bismuth electrode became more efficient the smaller the cation and the lower the electrolyte concentration. Cadmium quantification had to be performed using sodium hydroxide as the digestion media, as cations capable of supporting complete, facile biomass dissolution were found to be incompatible with ASV.

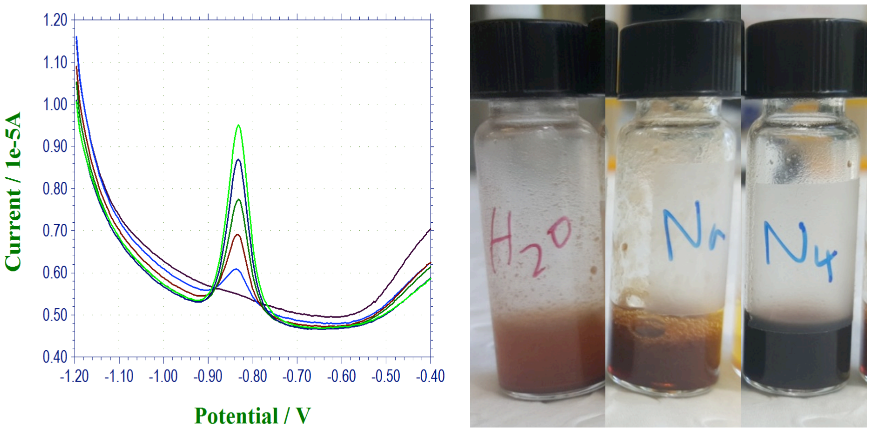

Figure: Left shows the square wave voltammetric ASV quntification of dissolved Cd at a bismuth electrode (between 8-40 µg/L Cd(II)), and **right** shows 2 wt% cocoa powder after being stirred in 1.5 M water (H_2O), 1.5 M NaOH (Na) and 1.5 M tetrabutylammonium hydroxide (N_4)

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Directly deposited PVP-Nafion nanofiber on sulfur cathode with enhanced electrochemical performance for lithium sulfur batteries

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Lithium-sulfur batteries have shown a great deal of potential in addressing the low energy density of lithium ion batteries due to the fact that sulfur cathode can deliver a high energy density of 2500 Wh/kg. However, the sulfur cathode has several critical issues to be solved before being applied to the commercial secondary battery. These issues are mainly caused by the dissolution of polysulfides during the electrochemical reaction, which results in shuttle effect and side reaction of lithium metal electrode. To address these challenges, we demonstrated a facile strategy of depositing the PVP-Nafion nanofibers directly on sulfur cathode by electro-spinning (e-spinning) method to localize the polysulfides species within the cathode area. The e-spinning precursor solution was prepared by dissolving the PVP with ethanol, followed by introducing Nafion into the solution. Then as-prepared solution was directly e-spinned on the sulfur cathode composed of pure sulfur, super P, and PVdF. The sulfur cathode with PVP-Nafion nanofiber layer exhibited better electrochemical performance than pristine sulfur cathode, owing to the efficient blocking of polysulfides to the anode side. We believe that our strategy of depositing the polymer-based nanofiber on cathode can be further extended into the other types of hybrid materials such as metal oxides, conducting polymer, etc.

Dual-wavelength Electrochemiluminescence Ratiometry for microRNA Detection

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Ratiometric electrochemiluminescence(ECL) assay, in which the quantification depends on the ratio of two signals instead of absolute values, has attracted wide attention. Based on the unique excitation potential and emission wavelength of ECL emitters, ratiometric ECL includes both dual-potential and dual-wavelength signal ratiometric assays. Dual-potential ratiometric ECL assay is based on two ECL emitting states that have the potential-dependent properties upon the substrate concentration. A few works addressing on the dual-potential ratiometric ECL systems in biological and chemical analysis have been reported. For dual-wavelength ratiometric ECL, no spectral overlap for the luminescence wavelengths of two ECL emitters is needed. However, restricted by the luminescence intensity and wavelengths of commonly used ECL emitters, dual-wavelength ratiometric ECL has not been developed yet. In this approach, a dual-wavelength ratiometric ECL approach is reported for the first time based on resonance energy transfer (RET) from graphite-like carbon nitride nanosheet (g-C_3N_4 NSs) as a donor to $Ru(bpy)_3^{2+}$ as an acceptor for sensitive microRNA detection. Here, Au nanoparticles (Au NPs) functionalized g-C_3N_4 NS nanohybrid (Au-g-C_3N_4 NH) coated on glassy carbon electrode (GCE) could exhibit strong and stable ECL emissions with emission peak centered at 460 nm. The ECL emission at such wavelength matched well with the absorption peak of $Ru(bpy)_3^{2+}$ as well as impeccably stimulate the emission of $Ru(bpy)_3^{2+}$ at the wavelength of 620 nm, producing ECL-RET with high efficiency. Thus, based on the ECL signals quenching at 460 nm and increasing at 620 nm, by measuring the ratio of ECL intensities at two luminescence wavelengths (460 nm and 620 nm), we could sensitively detect the concentration of target microRNAs in a wide range from 1fM to 1 nM. This work successfully breaks the bottleneck of the foundation and application of the dual-wavelength ratiometric ECL system and provides an important reference for the further study of ratiometric assay.

Oxygen reduction reaction at self-assembled monolayers of copper-based electrocatalysts on a polycrystalline Au electrode

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We report two-dimensional model systems to study electrocatalytic activities of dinuclear copper complexes [1,2] for various electrocatalytic reactions including the oxygen reduction reaction (ORR), where we can use electrochemical techniques as well as surface-sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and vibrational sum frequency generation (VSFG) spectroscopy. Heteroaromatic thiols including four 1,2,4-triazoles and a thiadiazole are used as metal ligands as well as anchors to a polycrystalline gold electrode. The thiols are self-assembled on the polycrystalline gold elecctrode and then react with copper(II) ions to give monolayers of copper-based ORR catalysts on the surface. The dinuclear copper complexes of 1,2,4-triazole-3-thiol (HDT) and 3-amino-1,2,4-triazole-5-thiol (ATT) show ORR activity and similar pH-dependent catalytic behavior to that of counterparts supported on carbon black, suggesting that our two-dimensional systems can serve as model catalysts for carbon-supported molecular catalysts [3]. We have also self-assembled dinuclear copper complexes with long alkyl or perfluoroalkyl chains on the surface and studied their orientation on the surface and oxygen transport.

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WO_3 Nanofibrous Backbone Scaffolds for Enhanced Charge Transport in Metal Oxide Semiconductor Photoanodes for Photoelectrochemical Water Splitting Hydrogen Generation

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Solar driven catalysis on semiconductors to produce a clean hydrogen fuel has been considered as a promising technology to mitigate environmental issues. In compare to single photoabsorber, the merits of hetrostructured semiconductor interfaces in producing large fraction of solar light photon harvesting to the photoelectrochemical reaction as well as rapid charge separation are anticipated to contribute high quantum yield of hydrogen generation in PEC cells. We report the electrospun derived WO_3 backbone fibrous channel for the improvement in the electron transport from the charge separation interface between the photoanode and electrolyte interface to the charge collector. Various metal oxides photoabsober layers such as TiO_2, Fe_2O_3 and $BiVO_4$ has been post-deposited on back bone WO_3 fibrous channels. Optical properties and JV characteristic were monitored to investigate PEC performances. External quantum efficiency of the PEC cells using these hetero structured photoanodes was examined using incident photon to current efficiency. The electrochemical impedance measurements were also conducted for analyzing the interfacial charge transfer at photoanode/electrolyte interfaces. As a result, $BiVO_4$ coated WO_3 heterophotoanode results high quantity of hydrogen generation compare to other structures. Our investigation provides understanding of PEC performances in heterostructured nanostructure based on WO_3. Therefore, readily available WO_3 fibrous electrodes can be transformed to any other hetero photoabsorbers and additional coating of co-catalyst will enhance the current PEC performances.

Production of Iron Particles Using Grape Leaves

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Production of nano metal particles using plants has become a major interest of relevant researchers in recent years. The techniques aforenamed are simple to apply, environmentally friendly, cost-effective and reproducible; Extracts of various plants or parts of plants such as leaves, root, latex, seeds and stems have been used as reductants. Some examples of these plants are green tea, black tea, coffee and grape leaves etc. The key active agent for these productions are believed to be polyphenols, present in the plant parts.

Iron nano particles are one of the most preferred targets because of environmental applications of zero valent iron, and also easy reduction of iron (III) salts to the zero valent forms. There are many reports on producing nano sized iron and iron oxides using plants and, the structures of nano particles have been identified by many investigators (1), (2).

0.1 M $FeCl_3$ solution as Fe source and grape leaves extract, which is produced from the extraction using %78 ethanol, as reducing agent have been used in this study.

Sizes of the particles produced were observed as about 100 nm. after the analyses using a Zetasizer (Malvern).

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3D structured $NiCo_2O_4$ nanorods on Co_3O_4 nanosheets and Jackfruit derived high surface area porous carbon as electrode for high energy asymmetric supercapacitor

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Abstract:

We report the fabrication of high energy asymmetric supercapacitor (ASC) using pseudocapacitive 3D microstructured composite $NiCo_2O_4@Co_3O_4$ and double layer forming activated carbon (AC). The pseudo capacitive electrode is synthesized *via* a facile two step hydrothermal process and AC is obtained from the bio-waste, Jackfruit (JF) peel by chemical activation. Extensive powder characterization and optimization has been conducted for both electrodes, especially in electrochemical aspect. The ASC is fabricated using JF derived AC as anode and $NiCo_2O_4@Co_3O_4$ cathode in aqueous media. Prior to the ASC assembly, the mass loading between the electrodes are adjusted based on the single electrode performance of both components *vs.* Ag/AgCl. The ASC is capable of delivering a maximum energy density of 42.5 Wh kg^{-1} at power density of 80 W kg^{-1}. In addition, the ASC rendered excellent cycleability, for example, the cell retains ~97% of initial capacitance after 7000 cycles. The outstanding performance of the ASC is originated from the well-developed building blocks of porous electrodes. An impedance study is also conducted to corroborate the excellent performance of $NiCo_2O_4@Co_3O_4$ *vs.* JF derived AC based ASC.

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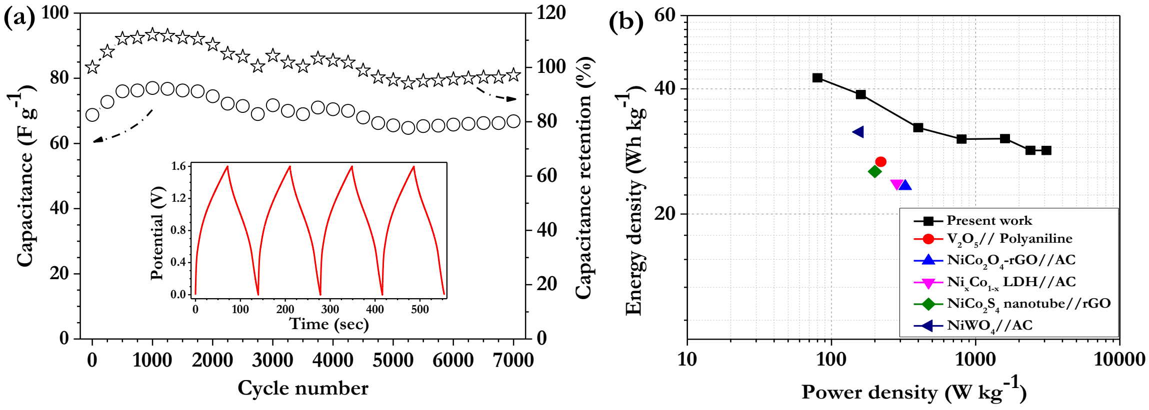
Figures:



(a) Cycling profiles of ASC at current density of 2 A g^{-1}, Inset: typical charge-discharge curves and (b) Ragone plot of $NiCo_2O_4@Co_3O_4$ *vs.* JF-2 based ASC with previously reported ASC. AC: activated carbon, LDH: layered double hydroxide, rGO: reduced graphene oxide.

DNA Labeling Generates a Unique Amplification Probe for Sensitive Photoelectrochemical Immunoassay of HIV-1 p24 Antigen

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Photoelectrochemical (PEC) immunoassay is an attractive methodology as it allows for an elegant and sensitive protein assay. However, advanced PEC immunoassay remains challenging and the established amplifications rely almost exclusively on the labeling of various enzymes, which usually suffer the inferior stabilities. Here we report the development and validation of the DNA labeling that leads to a unique amplification probe for the sensitive PEC immunoassay of HIV-1 capsid protein, p24 antigen, an important biomarker of human immune deficiency virus (HIV). Following the sandwich immunobinding, the DNA tags could be released and the subsequent dipurinization of the oligonucleotide strands enables the easy oxidation of free nucleobases at a CdTe quantum dots (QDs) modified ITO transducer. Such DNA tags induced PEC amplification and readout permits the exquisite assay of HIV-1 p24 antigen with high sensitivity. As compared to the existing method of enzymatic labeling, the easy preparation and stability of these labels make them very suitable for PEC amplification. Another merit of this method is that it separates the immunobinding from the PEC transducer, which eliminates the commonly existing affection during the biorecognition processes. This work paves a new route for the PEC immunoassay of HIV-1 p24 antigen and provides a general format for the PEC biomolecular detection by means of the DNA labeling.

Synthesis and Modification of Anodic TiO_2 Nanotubes

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The anodizing is a high-voltage electrochemical conversion process that forms barrier-type oxide layers or nanoporous/nanotubular structures on valve metals and alloys mainly depending on the composition of electrolyte used.[1] The key to achieve the ordered nanoporous/nanotubular structures is a displacement of the film material above the original surface position due to synergistic effect of pits generation (field assisted oxide dissolution), stress generated at the metal-oxide interface including electrostriction and plastic oxide flow switching the growth of the barrier-film to nanotube/nanopore. Typically, the TiO_2 nanotube array formed in organic electrolytes such as glycerol, dimethyl sulfoxide, ethylene-glycol is obtained in the form of close packed structure in which the nanotubes nearly stick together with the tube walls. A fundamentally different nanostructure from that is obtained in diethylene-glycol electrolyte. The nanostructure is characterized by free standing nanotubes separated by an interconnecting space larger than the diameter of nanotubes (Fig. 1).

Herein we report on how to control the synthesis of TiO_2 nanotubes to achieve wide spacing in between nanotubes. [2,3] We discuss functional properties of titania nanostructures and report the application of titania as a template material for electrodeposited nanostructures. We compare the template to anodic alumina oxide (AAO) which is one of the most widely used hard template materials; the secondary material is typically deposited in the pores of AAO forming nanowires of desired length and diameter. With TiO_2 nanotubes it is possible to control deposition inside the nanotubes and/or space in between them. The resulting electrodeposited nanostructes are in the form of: nanopore array, inverse nanotube array and nanowires. A general scheme for electrodeposition in TiO_2 nanotubes be presented. [4]

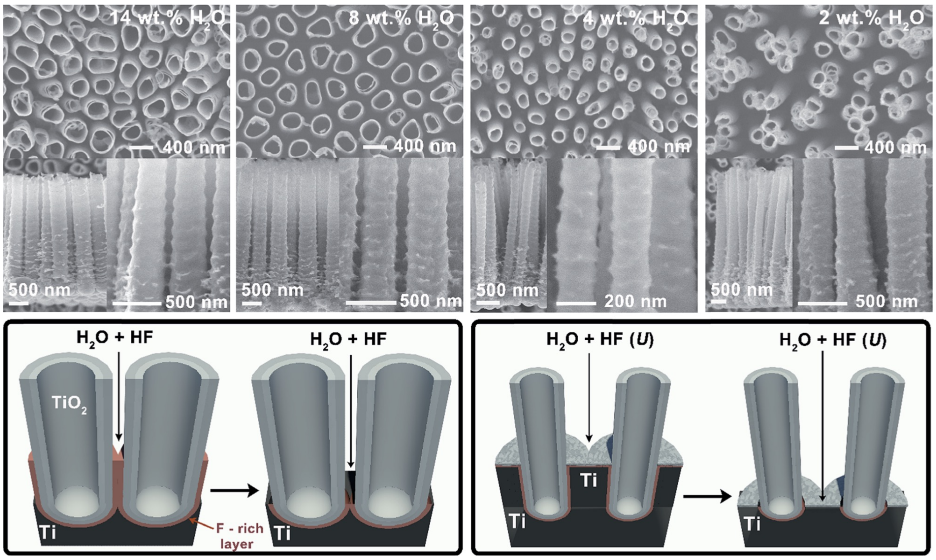

Fig. 1 SEM top and cross-section views for TiO_2 nanotubes formed at 60V for 16h in diethylene glycol electrolyte containing water content from 2-14 wt.%

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Control of localized galvanic corrosion between tungsten and titanium nitride during chemical mechanical planarization

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Galvanic corrosion between tungsten (W) and the titanium nitride (TiN) barrier layer inevitably occurs during chemical mechanical planarization (CMP), which led to the various defects (e.g., corrosion and pitting issues) at the W/TiN interface. To decrease these defects, we control the corrosion potential difference between W and TiN through the mixing of two corrosion inhibitors. The chemical roles of corrosion inhibitors in CMP slurry are investigated through open circuit potential (OCP) measurements, linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). Through these electrochemical approaches, we have found that two mixed inhibitor system can decrease the galvanic potential and current density. CMP results with W/TiN patterned structures show that they prevent galvanic corrosions at the W/TiN interface during CMP, resulting in a significant decrease in defects. We believe that the results investigated in this study will provide researchers with the importance of electrochemical approaches in W CMP.

Lead Selenide Nanoribbons Synthesized by Galvanic Replacement of Lithographically Patterned Nickel Electrodes

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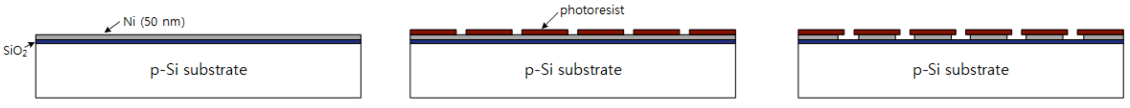
Thermoelectric materials which could regenerate waste-heat into usable electrical energy have been intensively investigated to achieve high thermoelectric properties described as dimensionless figure of merit, zT. To attain high zT value, materials need to hold high value of electrical conductivity and Seebeck coefficient and low thermal conductivity. Previously, PbSe was thought to be considerably inferior to PbTe as a thermoelectric material because of its higher thermal conductivity and lower band gap despite of its cheaper price. However, recent works revealed potentials of heavily doped PbSe as a competent thermoelectric material. The lattice thermal conductivity of PbSe becomes nearly as low as PbTe at high temperature and the bandgap of PbSe increases rapidly with temperature, even exceeding that of PbTe above 500 K. On the other hand, nanostructuring of materials such as superlattices, nanowires and nanoribbons could derive similar effects with doping process mainly by phonon-boundary scattering and quantum-confinement effect. In this work, we synthesized lead selenide nanoribbons by galvanic displacement reaction with an expectation of aforementioned effect. The fabrication process flow chart is shown in Figure 1. First, 50 nm-thick Ni sacrificial layer was deposited by e-beam evaporator on top of SiO_2 insulating layer. After that, a photoresist was spin coated and line-patterned by photolithography an etching mask. The underlying Ni layer would be over-etched by 0.8M HNO_3 etchant and the undercut was formed along the edge of photoresist line patterns. In order to synthesize PbSe nanoribbons, the exposed side walls were galvanically synthesized. Finally, remaining photoresist and nickel sacrificial electrodes were etched away totally. The width and thickness of nanoribbons could be controlled by the time of galvanic displacement reaction and nickel thickness, respectively. The synthesized nanoribbons were confirmed by scanning electron microscopy as shown in Figure 2 and detailed results such as correlations between thermoelectric properties and nanoribbon's size and composition would also be presented.



(a) evaporate 50 nm-thick Ni layer for a working electrode

(b) form the line patterns by photolithography

(c) wet etch the exposed Ni layer by 0.8M HNO_3 to form undercut

(d) galvanic displacement reaction of exposed Ni to form PbSe nanoribbons

(e) strip photoresist and Ni electrodes

Figure 1. Lead selenide synthesis by galvanic displacement reaction flow chart

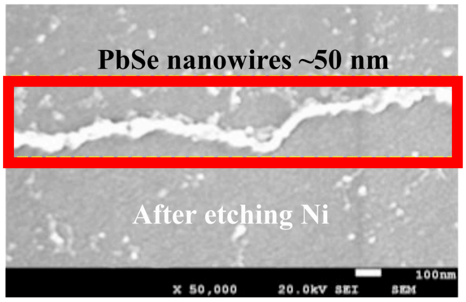


Figure 2. The SEM image of lead selenide nanoribbons

New approach to investigation of electrochemistry stability of carbon supports: ^{14}C accelerator mass spectrometry

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It is known that during operation of the PEMFC as a power source for an electric vehicle the local value of the cathode potential can reach up to 1.5 V [1], which is much higher than the potential of carbon oxidation. Therefore, the durability of the PEMFC is determined primarily by the corrosion resistance of carbon support in the Pt/C catalyst for the the oxygen electroreduction reaction (ORR). To investigate the electrochemical corrosion resistance of catalysts an accelerated testing protocols ("Start-Stop cycling") in a standard three-electrode electrochemical cell was developed [2].

Recently, it was shown that the Pt/C catalyst for the ORR based on carbon black KetjenBlack DJ-600 support modified with pyrocarbon exhibited higher corrosion resistance as compared to the unmodified analogue [3, 4]. Thus, the influence of the carbonization degree on the electrochemical corrosion resistance of the KetjenBlack DJ-600 support was studied in this paper.

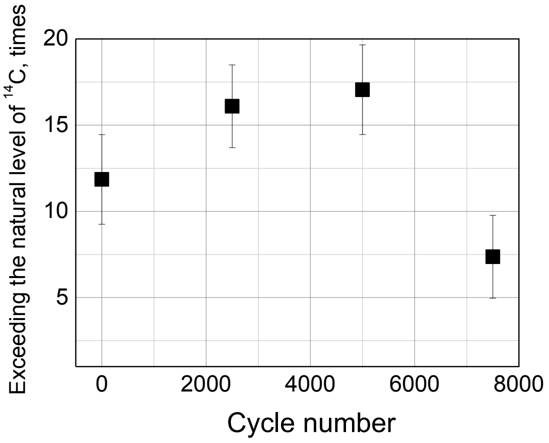

Fig. 1. Dependence of ^{14}C concentration in pyrocarbon-modified KetjenBlack DJ-600 from cycle number in "Start-Stop cycling" protocol.

The pyrolytic carbon deposition was carried out at 900 °C in a quartz reactor in methane stream during 5 - 65 minutes. Initial and modified KetjenBlack DJ-600 were investigated by the complex of physical and chemical methods, including XPS, element analysis, low temperature adsorption of nitrogen, cyclic voltammetry etc.

It was shown that the increase in the carbonization degree of the sample results in the higher electrochemical corrosion resistance.

In order to evaluate the reasons of the improved electrochemical stability upon modification with pyrolytic carbon, a series of experiments of the "Start-Stop" electrooxidation of the sample modified with ^{14}C-pyrocarbon was performed. Accelerator mass spectrometry (AMS) analysis results (Fig. 1) indicate that the electrooxidation of the pyrocarbon modified carbon black proceeds in three steps. In the first stage an increase in the ^{14}C content is observed, which is related to a higher electrochemical stability of pyrocarbon, leading to high-priority oxidation of pristine carbon black. The next stage is a pseudo-stable region. Further drop of the ^{14}C concentration is associated with the degradation of both the pyrocarbon and carbon black species in the composite sample.

Acknowledgments

This work was performed within the framework of the joint Research and Education Center for Energy-Efficient Catalysis of the Novosibirsk State University and the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences and supported by the Russian Foundation for Basic Research (grant no. 13-03-01023).

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Gas Sensing in Ionic Liquids on Miniaturised Electrodes: Screen-Printed Electrodes, Thin-Film Electrodes and thin Ionic Liquid Layers

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Amperometric Gas Sensors (AGSs) are routinely used for the detection of redox active gases, but are often limited in their applications under hot and dry conditions due to evaporation of the solvent (e.g. water). As a result, room temperature ionic liquids (RTILs) have been extensively investigated in the last ten years as replacement solvents in AGSs.[1,2] Their non-volatility has allowed them to be suggested as solvents in "membrane-free" gas sensors, where the elimination of the membrane could result in faster response times.[1] In order to reduce cost and miniaturize the sensing system further, planar devices, such as screen-printed electrodes (SPEs), thin-film electrodes (TFEs) and thin-film microarray electrodes (TFMAEs) have recently become commercially available (e.g from companies such as DropSens and MicruX). They typically consist of three electrodes screen-printed or sputter-coated onto a planar inert substrate. The electrodes are then connected either by immersing the electrode directly into the solvent, or by dropcasting a microliter quantity of solvent (e.g. 2-10 μL in the case of RTILs). The miniaturized sensing surface is exposed to an analyte gas, which partitions into the ionic liquid, and diffuses to the working electrode where it is detected.

In this presentation, we discuss some of the recent work on the electrochemical detection of oxygen and a number of toxic gases (e.g. ammonia, methylamine, chlorine, hydrogen chloride) in ionic liquids on miniaturized sensing surfaces. Unusual voltammetry for oxygen reduction was observed on Pt SPEs in imidazolium RTILs, suggesting a reaction of the electrogenerated superoxide with materials in the binding paste of the SPE in the slightly acidic ionic liquid environment.[3] No such reaction was observed[4] on Pt thin-film electrodes (made entirely of metal), where TFEs from MicruX gave a response similar to that on "ideal" Pt macrodisk electrodes. However, most of the other toxic gases showed similar electrode reaction mechanisms on SPEs, TFEs and conventional disk electrodes, suggesting that SPEs are a suitable sensing surface. Microarray TFEs have also been employed for oxygen and ammonia gas sensing using voltammetry and chronoamperometry. The sensor has also been made highly robust by combining the RTIL with the polymer poly(methyl methacrylate) (PMMA), and the response time has been improved by spin coating thinner PMMA/RTIL layers. These results will be presented.

The most important observation of our work is that it is possible to detect concentrations of toxic gases below their long-term exposure limits (e.g. 25 ppm for ammonia, 10 ppm for methylamine and 5 ppm for hydrogen chloride) on these miniaturized sensing surfaces in ionic liquids, without the need for any pre-concentrators, mediators or other measuring techniques.[5] This allows these cheap, mass-produced, miniaturized sensing surfaces to be used with very small quantities of RTILs for sensitive toxic gas sensing.

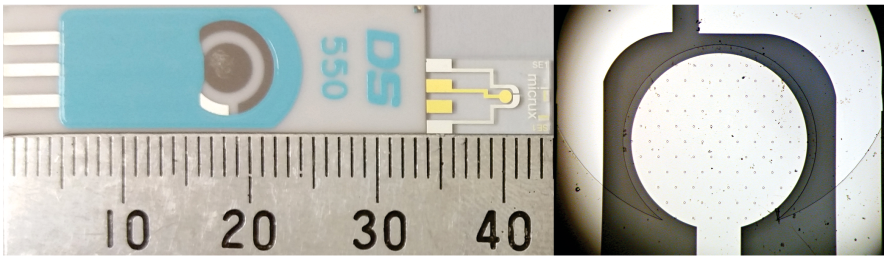

Figure 1: Left: size comparison of a SPE (DropSens) vs. a TFE (MicruX). Right: MATFE (MicruX)

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Effect of Anchoring Chemistry on Charge Transport through Au/Molecule/HOPG Junctions

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Molecular electronics aims to construct functional molecular devices at the single-molecule scale. One of the major challenges is to construct a single-molecule junction and to further manipulate the charge transport through the molecular junction. Break junction technique such as scanning tunneling microscope break junction (STM-BJ) is an ideal testbed to study the charge transport through single-molecule junctions. Repeating the formation-and-break junction cycles hundreds or to even thousands of times allows a statistical analysis of the data that overcomes the problem of data scattering due to variations in single-molecule junction configurations and provides statistically significant information concerning charge transport properties. Numerous break-junction studies were carried out to investigate charge transport through individual molecules in contact with gold electrodes (see e.g. [1]). However, the usage of sp^2-carbon-based electrodes for break-junction experiments is very scarce [2-4]. In this work, we form molecular junctions in the STM-BJ configuration, using a gold STM tip and highly oriented pyrolytic graphite (HOPG) as a substrate (Figure 1a). We explore the effect of anchoring on the conductance of single molecule junction: covalent *vs.* non-covalent. For the covalent modification of an HOPG surface, we use electrochemical grafting of diazonium salt derivatives: 4-nitrobenzenediazonium (NBD) and 3,5-dimetylbenzenediazonium (DMBD) tetrafluoroborate. Since nitro-group is known to be a poor linker for gold electrodes, we further electrochemically reduce grafted molecules to obtain amines. The modified HOPG surfaces were examined by STM imaging and Raman spectroscopy. In agreement with previous results [5], the grafting of NBD leads to dendrimer growth (Figure 1b); while for DMBD multilayering is avoided due to methyl groups protecting *meta*-positions (with respect to diazonium group, Figure 1c). The single molecule conductance of grafted molecules as obtained in STM-BJ measurements and estimated in DFT calculations is compared with the conductance of *p*-phenylenediamine (PDA, Figure 1d) non-covalently interacting with HOPG substrate. We also demonstrate that conductance of molecular junctions under study displays a strong bias-voltage dependence (in agreement with our DFT): the conductance significantly increases with increasing bias due to the vanishingly low density of states of HOPG around Fermi energy.

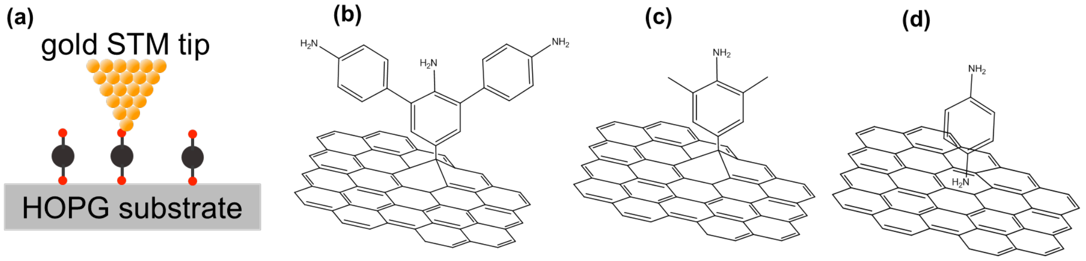

Figure 1. (a) Scheme of STM-BJ configuration. (b-d) Topmost layer of HOPG modified with (b) NBD, (c) DMBD, and (d) PDA. See details in the text.

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High Throughput Screening of Ternary Quantum Dots Sensitized Solar Cell: An Scanning Electrochemical Microscopic Investigation

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Solar energy is the most abundant nature resource and plays important roles in the sustainable developments of energy and environment. Scanning photoelectrochemical microscopy provides a high-throughput screening method by introducing the combinatorial technique to prepare the substrate with photoelectrochemical catalyst array. However, the signal/noise (S/N) ratio suffers from the background current of indium−tin oxide or fluorine-doped tin oxide itself, including a transient charge−discharge current of electric double layer and a steady-state photocatalytic current.

First, we propose a facile microfabrication method to isolate the substrate area other than the catalyst array from not only the electrolyte solution but also the light illumination. Consequently, the imaging quality has been promoted dramatically due to suppressed background current. This method provides a high S/N ratio screening method, which will be valuable for the highthroughput optimization of the photoelectrocatalytic system.

Second, we applied this method to screening of ternary quantum dots sensitized solar cell. The combinatorial methods was used to design the catalyst array of ternary quantum dots $Cd_xPb_{1-x}S$ solid solution, which is modified on the surface of TiO_2 nanoparticles as sensitizer through SILAR processes. The effects of precursor solution components and SILAR processes on the performance of photoelectric conversion were investigate. And the formula for the preparation of the quantum dots sensitized solar cell was optimized rapidly. The device experiments demonstrated the validity of the SECM screening results. A short circuit current density of 24.47 mA/cm^2 and a photovoltaic conversion efficiency of 5.33% were achieved.

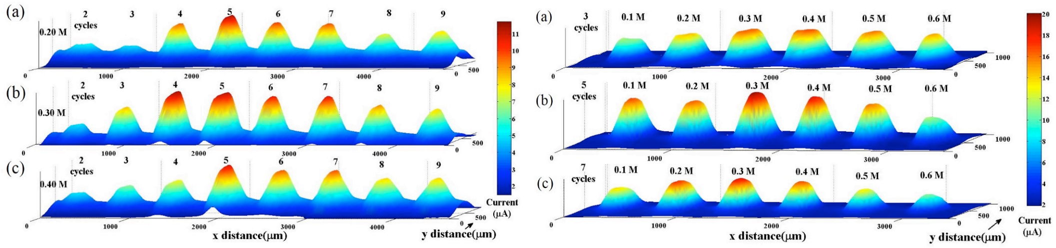

Figure 1. The effects of precursor solution components and SILAR processes on the performance of photoelectric conversion.

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Conducting Polymers Nanoparticles Based Electrochemical Sensors

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Nanostructures of conducting polymers have drawn research attention in recent years, with a special emphasis on applications[1]. However, the methods for conducting polymer (most often polypyrrole or polyaniline) nanoparticle synthesis most often require application of matrices, either soft or hard. As a consequence the surface of resulting nanoparticles is compromised – the charge and/or ion exchange between nanoparticles and environment is hindered. Thus the application of conducting polymers nanoparticles: e.g. polypyrrole, for benefits of electrochemical sensors has not been widely considered.

The recently proposed by us template method yields nanoparticles of narrow size distribution and high electrochemical activity due to active unblocked surface[2]. Thus obtained stable water suspensions of nanoparticles of conducting polymers are highly attractive material for electrochemical sensors preparation. Different model systems have been tested to highlight the benefits of application of conducting polymers nanoparticles of high electrochemical activity for electrochemical sensors:

(i) disposable ion selective electrodes, in which conducting polymer nanoparticles are used as electrical lead and transducer, and are covered by ion-selective membrane;

(ii) electrolyte-gated carbon nanotube field-effect transistors in which gate has been modified with ion-selective membrane composition enriched with nanoparticles;

The water suspension of conducting polymer nanoparticles were applied on paper (manually or using automatized approach) to yield the conducting track that can be used to construct ion-selective electrodes. The part of the conducting track was used as electrical lead and the part was further modified with classical ion-selective membrane cocktail to yield disposable ion-selective electrodes. Thus obtained sensors, e.g. potassium selective electrodes, where characterized with excellent analytical performance in terms of slope and selectivity. The good reproducibility of electrode standard potential was also achieved. Thus herein described sensors are highly promising alternative, compared to e.g. those based on carbon nanotubes, proposed in literature.

For transistors the ion-selective membrane composition modification with nanoparticles of conducting polymers has led to substantial improvement of performance compared to the sensors with unmodified ion-selective membrane. The pronounced increase in recorded currents contributes to higher sensitivity of determination as shown on the example of potassium ions sensors.

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Optimization of parameters of conducting polymer solid contact ion-selective electrodes

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All-solid-state ion-selective electrodes (ASS-ISEs) with conducting polymer solid contact represent good analytical parameters, comparable with those of classical sensors with internal filling solution. Significant parameters characterizing quality of the solid contact, related to ion-to-electron transduction, is the electrical capacitance of the solid contact [1] and reproducibility of the recorded potentials.

In many cases the capacitance of the solid contact is lower than for the solid contact only, in the absence of ion-selective membrane (e.g. [2,3]). This effect can be disadvantageous, particularly for sensors working under polarization conditions, in galvanostatic mode.

The effect of capacitance lowering was studied on example of model systems of anion- and cation-selective electrodes with poly(3,4-ethylenedioxythiophene) (PEDOT) solid contact with anion- or cation-exchange properties. Basing on results obtained for these membranes and contacts as well as on some model calculations, the reasons of reduced capacitance were ascribed to low amount of ions transferrable across the solid contact / membrane interface. This effect can result from low concentration of mobile ions in the conducting polymer contact / ion-selective membrane or low rate of ion transfer. Therefore, in this work new procedures or pretreatment methods were proposed to minimize the effect of capacitance decrease.

Additional improvement of ASS-ISEs parameters can be obtained by incorporation to the highly capacitive material of the solid contact a redox couple immobilized within the contact phase [4]. This modification should result in potential stability and thus better reproducibility of the potentiometric responses of the sensor. This effect was checked on example of PEDOT with selected redox couples and improvement of potential stability was obtained.

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Specific electro-oxidation of cellulose at carbon/AuNPs electrocatalysts

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Introduction:

A scientific and technological breakthrough in innovative utilization of cellulosic biomass offers tremendous possibilities to establish a sustainable society. Electrochemical oxidation of cellulose at an Au electrode surface offers a new route for the transformation of cellulosic biomass to functional materials as alternatives to petrochemical products. The new electrochemical reaction route to oxidize cellulose molecules at an Au electrode surface was discovered a few years ago.[1] Moreover, the mechanism of the reaction occurring on a pristine bare Au electrode surface has been under detailed investigation in recent years.[2] It has been suggested that the electrochemical processes occurring on an Au electrode can also be applied in direct oxidation and functionalization of hemicellulose molecules.[3] It is expected that the electrochemical reaction process of polysaccharides, including cellulose and hemicelluloses, can be altered by controlling the electrode/electrolyte interface.

Objective:

In this work, new electrochemical properties of cellulose at a carbon electrode decorated with Au nanoparticles is described. The influence of the size and the oxidation state of Au nanoparticles on the specific direct electro-oxidation of cellulose is investigated.

Materials and methods:

Carbon paper electrodes modified with gold nanoparticles (AuNPs) were used as electro-catalysts (carbon/AuNPs) for the electrochemical oxidation of 1 % (w/v) cellulose dissolved in 1.3 M NaOH. The size and oxidation state of the AuNPs were determined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Both the size and the oxidation state of the AuNPs were found to influence the electro-catalytic properties of the electrode, as studied by cyclic voltammetry (CV), square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS).

Results and discussion:

Results suggest that cellulose molecules were oxidized in an alkaline medium on carbon/AuNPs electrocatalyst consisting of Au^0. The electro-catalytic activity upon oxidation of cellulose is higher when the size of AuNPs is less than 25 nm and the nanoparticles consist of Au^0 only. Moreover, a new oxidation process at ca. 0.2 V was observed which was not observed at a polycrystalline bare Au surface. It is indicated that both the size and the oxidation state of AuNPs are key parameters for determining the specific electro-catalytic oxidation of cellulose at an electrode interface. This research work may provide an additional new reaction pathway offering new routes towards a series of functional materials derived from polysaccharides.

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Photoelectro-Catassembly of Two-dimensional Polymer

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Abstract: Recently inspired by catalysis, we propose a specific mode of assisted molecule assembly. A new term, ‘‘catassembly,’’ is suggested to refer to the increase in the rate and control of a molecular assembly process. This term combines the words ‘‘catalysis’’ and ‘‘assembly,’’ and identifiably retains the Greek root ‘‘cat-’’ of catalysis, referring to the ‘‘helper’’ species. Catassembly in molecular assembly is a concept analogous to catalysis in chemical synthesis. Because most efforts in the field of molecular assembly have been devoted to the design and synthesis of molecular building blocks, we wish to stress the apparently missing yet critical link to complex chemical systems, i.e., the design and utilization of molecular catassemblers to facilitate the formation of functional molecular assemblies from building blocks with high efficiency and selectivity. We hope this rational control and accelerated method will promote the systems chemistry approach, and may expand the spectrum of molecular assembly from basic science to applications.

The new field of catassembly can learn from the well-established field of catalysis including its branches such as electrocatalysis and photo-electrocatalysis to develop future methodologies. The catassembly can occur at the liquid/solid interface and realize the heterogeneous catassembly, it’s highly desirable to develop some new approaches. Here, we report the photoelectro-catassembly of two-dimensional polymer (molecule assembled layer) from electrode based on the synergy of potential-controlled assembly/disassembly and photo-induced reaction (Figure 1). The molecule-modified electrode first serves as an electro-assisted template with positive potential to form the molecular double layer, then the upper layer with the building blocks is polymerized through photoreaction and further is removed from the template by the control of negative potential. Thus, the molecule-modified electrode assisted the synergistic process as a photoelectro-catassembler and it works repetitively to produce 2-D polymer like a “molecular printer”. This strategy of photo-electrochemically catalyzed molecule assembly may pave the way toward the effective constructions of complex 2-D functional materials.

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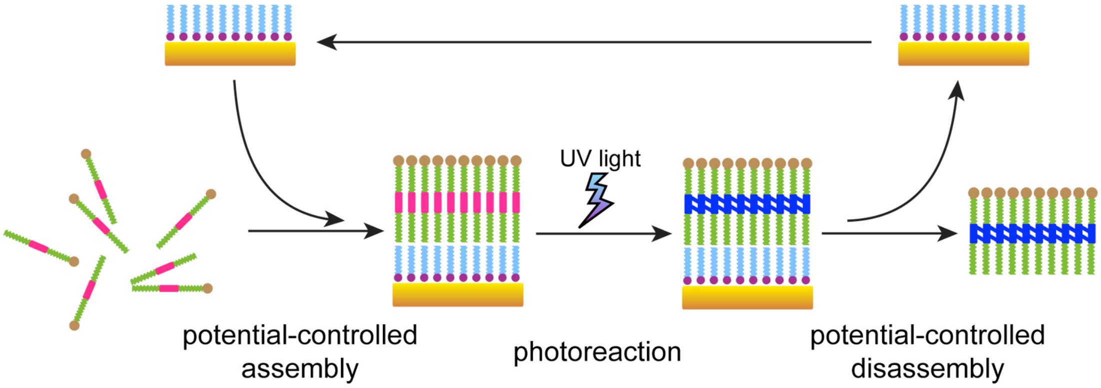

Figure 1. Schematic of photoelectro-catassembly of two-dimensional polymer. Building blocks are first adsorbed by the molecule-modified electrode (self-assembled monolayer on gold) under potential control, forming the 2-D assembly with non-covalent interactions (π–π stacking in the red segments). Then the UV irradiation is applied to form 2-D polymer by turning the non-covalent interactions into the covalent interaction (blue segments). Finally, the 2-D polymer is removed from the electrode under potential control, releasing the electrode for the repetitive assembly of building blocks.

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Porous graphite-like carbon nitride nanosheets (g-C_3N_4-OH/COOH) for electrochemical determination of copper ions at femto-mole level

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The functional modification of bulk graphite-like carbon nitride (g-C_3N_4) with strong oxidant, such as $KMnO_4$ and concentrated sulfuric acid, is a novel synthetic method for porous functionized g-C_3N_4 nanosheets (g-C_3N_4-OH/COOH), which can attach hydrophilic groups, like –OH and –COOH, onto the basic g-C_3N_4. This novel carbon nitirde has many unique features, including the three-dimensional and cellular structure, and the high specific surface area, which aids its excellent disbursement in aqueous solutions. Moreover, g-C_3N_4-OH/COOH showed significantly enhanced adsorption capability of copper ions and extremely sensitive electrochemical responses compared with the bulk g-C_3N_4 and the detection limit of the electrode coated by g-C_3N_4-OH/COOH was 1.0×10^{-16} mol/L, which realized proper femto-mole level electrochemical analysis of copper ions for the first time. These results highlight the crucial role of the morphology and attached functional groups on the electrochemical performance of carbon nitrides.

In this abstract, through a simple synthetic method using g-C_3N_4 as a raw material, we first obtained a functionalized graphite-like carbon nitride containing hydrophilic groups in its irregular, three-dimensional cellular ultrastructure, which was named as 'graphite-like carbon nitride attached by –OH and -COOH' (simplified as g-C_3N_4-OH/COOH) (Figure 1, 2).

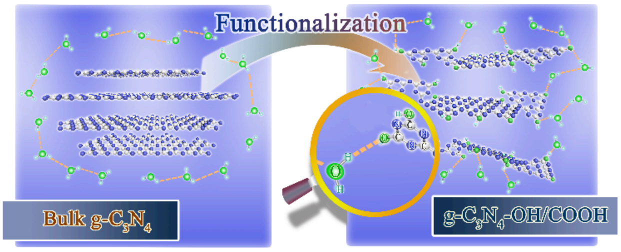

Figure 1. Schematic illustration of the functionalization to bulk g-C_3N_4 and the introduced hydrophilic groups into g-C_3N_4-OH/COOH.

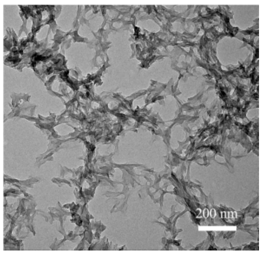

Figure 2. TEM image of g-C_3N_4-OH/COOH.

Owing to its irregular, three-dimensional cellular ultrastructure, structurally added hydrophilic groups and, thus, higher specific surface area and good dispersibility in aqueous solution, cyclic voltammetric (CV) measurements were performed for g-C_3N_4 and g-C_3N_4-OH/COOH in the presence of 7.6×10^{-6} mol/L Cu^{2+} at a scan rate of 0.05 V s^{-1} to examine whether the as-prepared material had a better electrochemical performance. Compared with bulk g-C_3N_4, a remarkable anodic current peak centered at -0.02 V was observed for g-C_3N_4-OH/COOH/GCE in the presence of Cu^{2+} (Figure 3). The above results verified that g-C_3N_4-OH/COOH exhibited an excellent electrochemical performance for detection of Cu^{2+}, which could be attributed to its high specific surface area and the hydrophilic groups introduced by functionalization.

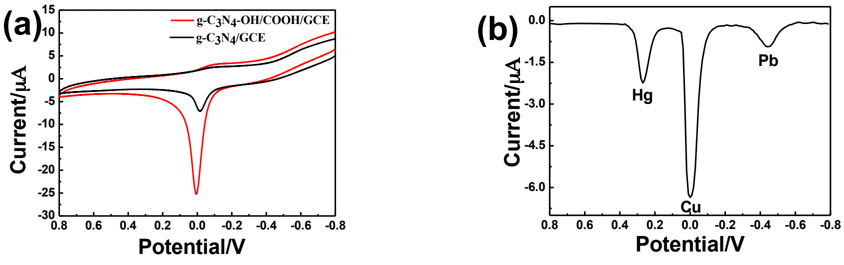

Figure 3. (a) CVs of different electrodes in 0.05 mol/L PBS at pH 4.68 in the absence and presence of 7.67×10^{-6} mol/L Cu^{2+}. (b) Influence of interference ions on the peak current in buffer solution containing 6.49×10^{-8} mol/L Cu^{2+}.

High aqueous dispersion stability manganese oxide-modified graphite electrode for stable and high performance lithium ion battery

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Graphite is a well-known active material as an anode in lithium ion batteries due to their low cost, good reversibility, and cycle stability. However, the relatively low theoretical capacity of graphite makes it challenging to apply graphite anode to next generation lithium-ion batteries. To address the problem of graphite anode, transition metal oxide-based anodes are intensively investigated. Manganese oxide (MnO_2) is one of the promising transition metal oxide-based anode materials due to its high theoretical capacity of 1233 mAh/g. Here, we investigated the novel strategy for preparing the surface modified graphite using MnO_2 (M-graphite) as a lithium ion battery anode material, which shows high specific capacity. MnO_2 layer not only provides hydrophilicity to the graphite electrodes which can improve processability and electrolyte percolation, but also contributes the additional capacity by MnO_2. With our novel strategy, surface modified graphite anode yields higher electrochemical performances with stable cycle performance, compared to the pristine graphite. We believe that our approach can provide the facile breakthrough via surface modification using metal oxide in the field of high energy density rechargeable batteries.

Study of electrochemical performance of Li_2FeSiO_4/C high-voltage cathode material at high temperature

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Abstract

The Li_2FeSiO_4/C (so-called LFS/C) high-voltage cathode material was synthesized by a sol-gel assisted solid-state method using Fe_2O_3, Tetra-ethyl orthosilicate (TEOS), and lithium acetate. The sucrose was used as a carbon sources. The LFS/C cathode material was sintered at 600-700°C in an Ar atmosphere for 10-12 h. It was found that the particle size of Fe_2O_3 and TEOS hydrolysis conditions play an important role in the synthesis process. It was found that the pH value of TEOS hydrolysis is critical; it needs to well control to avoid impurity phase occurred. The physical and chemical properties of the as-prepared LFS/C cathode materials were examined by XRD, SEM, TEM, micro-Raman spectroscopy, and EA. The electrolyte with 1wt.%FEC additive was also examined. The Li_2FeSiO_4/C cathode material with electrolyte+1wt.%FEC showed the discharge capacities of 203.4 mAh g^{-1} at 45°C (0.1C) and 211.9 mAh g^{-1} at 55°C (0.1C). In contrast, he discharge capacities of the Li_2FeSiO_4/C cathode material for 45°C and 55°C at 1C rate by using the electrolyte+1wt.%FEC are 126.6, and 137.3 mAh g^{-1}, respectively. The high temperature performance of LFS/C composite material was studied in detail. In conclusion, it was revealed that the best electrochemical performance and cyclic stability of the Li_2FeSiO_4/C composite cathode material was using 1M LiBOB in EC:DEC +1wt.%FEC electrolyte. It was found that our-prepared spray-dried spherical LFS/C cathode material shows a good performance at elevated temperatures of 45°C and 55°C.

Keywords: Li_2FeSiO_4/C, High-voltage cathode material, High temperature, Fluoroethylene carbonate (FEC), Cyclic stability

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In situ studies of the Growth and Pitting behaviour of the Passive film on Iron at Mildly Elevated Temperatures

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The composition and morphology of the passive film on iron were investigated at temperatures between 22 °C and 48 °C, after growth by potentiodynamic polarization in 0.05M NaOH and during pitting after addition of 0.05 M NaCl. Raman spectroscopy with pre-Resonance enhancement was used to monitor the composition of the film in situ after addition of the chloride and during chronamperometric measurement of the pitting potential. The morphology and composition of the film were examined ex situ using SEM (Scanning Electron Microscopy) and Grazing Incidence X-ray Diffraction.

Changes in the morphology of both the inner and outer layers of the passive film were observed as the electrolyte temperature was elevated. As shown in the SEM images in Figure 1, the structure of the outer layer formed after 15 cycles of potentiodynamic polarization comprises tightly packed, randomly oriented platelets. The diameters of these platelets were observed to increase in size with increasing temperature, almost doubling from approximately 100 nm at 22 °C to around 200 nm at 48 °C. The change in temperature also resulted in shifts to lower potentials of the anodic and cathodic current peaks.

MCR-ALS (multivariate curve resolution with alternating least squares) has been used in previous studies to identify the iron oxide compounds present from Raman spectra collected in situ of the passive film: at different stages during its growth by potentiodynamic polarization[1] and during its localized breakdown upon addition of chloride[2]. In this study, the same techniques were used to characterize the composition of the passive film grown at more elevated temperatures between 22 °C and 48 °C.

The effect of temperature on the potentiodynamic polarisation curves, the pitting potential and the crystallinity and composition of the passive film are discussed.

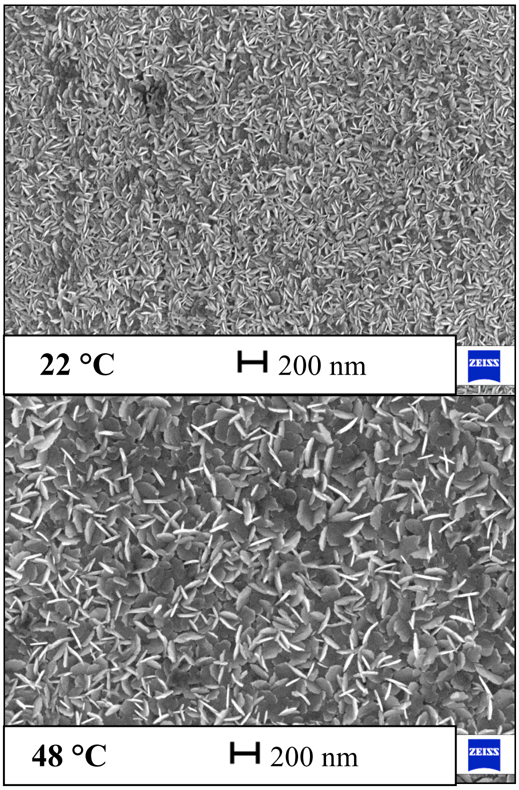

Figure 1. SEM images of the passive film on iron after growth by 15 cycles of potentiodynamic polarizatyion in 0.05M NaOH, at 22 °C (top) and 48 °C (bottom).

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Rare earth (Re=La, Ce, Eu, Tb) doped Ta_2O_5 materials and study on their electrocatalytic activity

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The utilization of non-platinum catalyst is the effective approach to achieve the high performance electric catalyst by reducing the cost of noble metal. Ta_2O_5 is a stable oxide in both acidic and alkaline solutions, and thin Ta_2O_5 films are semiconductors, suggesting it has promise for application in electrodes. In the present work, a series of rare earth (Re=La, Ce, Eu, Tb) doped Ta_2O_5 film electrode material were prepared in an effort to improve the electrocatalytic activity of Ta_2O_5.

Rare earth doped tantalum oxide (Re doped Ta_2O_5) particles were synthesized using a low temperature hydrothermal method Re doped Ta_2O_5 (Re=La, Ce, Eu, Tb). The crystal phase of the samples was analyzed using X-ray diffraction (XRD). The result revealed that the Re doped Ta_2O_5 particles had a good crystalline structure of the orthorhombic phase with no any impurities peaks. The peak shifts to the higher angles were observed after doping Rare earth (R=La, Ce, Eu, Tb), indicating contractive cell of Ta_2O_5 via the doping of rare earth. The electrocatalytic activity of Re-doped Ta_2O_5 film electrode was investigated by cyclic voltammetry (CV) in 0.5 mol L-1 H_2SO_4 solution. It indicated that the electrocatalytic activity of La doped Ta_2O_5 larger than that of Tb doped Ta_2O_5 film electrode. Meanwhile La doped Ta_2O_5 exhibited excellent electrochemical stability, which is even better than Pt/C or pure Pt electrode.

Corrosion is not always bad – using corrosion-like processes to remove poisons on electrocatalysts

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Corrosion-like processes can be used to effectively and quantitatively remove a range of poisons which block crucial electrocatalytic processes such as the hydrogen oxidation reaction (*hor*) and the oxygen reduction reaction (*orr*). These reactions are critical in the operation of low temperature fuel cells, and poisoning of the Pt/C catalysts in these systems represents one of the processes which ultimately limit the operation of these systems. Such catalyst performance degradation may be due to exposure to environmental pollutants, especially those present in either the fuel source, or in the air drawn into the fuel cell. Although the issue of contaminants in the ***fuel*** can be dealt with as the source of fuel is controlled, there may be a large cost associated with providing sufficient pure fuel, or the fuel may be contaminated *en route* to the fuel cell. For the air source, the situation is even more difficult as the source of ***air*** is not controlled, and this pathway represents a potent potential source of contamination. Although some work has been previously performed on mitigating catalyst poisoning in electrochemical cells, these electrochemical approaches are typically very inefficient and poorly suited to single cell fuel cells and ineffective in fuel cell stacks. Faced with an inability to recover a fuel cell stack, the only other solution is to replace the stack – at great cost. Hence the ability to quickly and easily remove contaminants degrading catalyst performance in fuel cells is an important scientific and commercial goal. Such an approach would then be universally applicable to electrochemical cells, single cell fuel cells and stacks.

Recently, we have examined the use of ozone to chemically clean catalysts poisons from platinum electrode surfaces[1]. In this paper we show that the process is scalable from electrochemical cells, to single cell fuel cells to fuel cell stacks, and applicable to both anode and cathode containments. The process appears to rely on a local coupling of the electrochemical reduction of ozone along with the electrochemical oxidation of the contaminant, figure 1(a). Reaction with ozone leads with sulfur deactivated catalysts result in a large jump in the opencircuit voltage of the electrode (figure 1(b)), matched to production of sulfur dioxide, figure 1(c). The process can even be applied to fuel cell stacks to recover a poisoned system, figure 1(d).

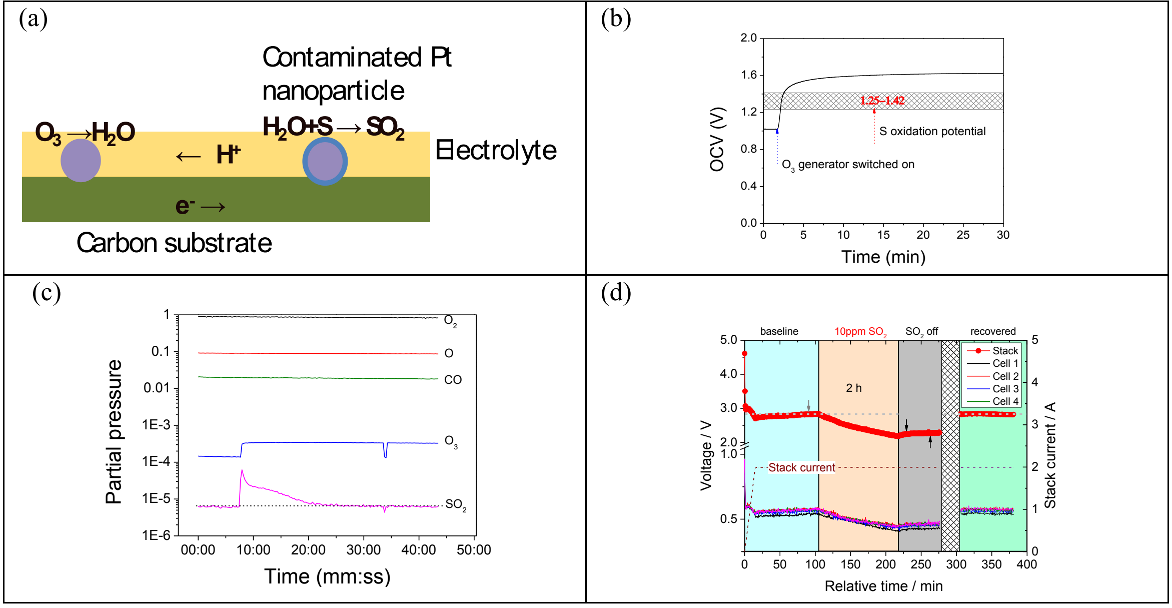

Figure 1. Examples of catalyst poisoning and recovery. (a) cartoon showing the corrosion like removal of a poison from the Pt/C catalyst surface. (b) OCV with time for a sulfur poisoned Pt/C catalyst in 0.1 M HClO4; (c) Trace showing production of SO_2 during exposure of a S-poisoned single cell fuel cell to ozone; (d) example of poisoning and recovery of a five-cell fuel cell stack with ozone.

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Study of the electrical double layer at the solid (304L) / liquid (NaCl solution) interface

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Keywords: Electrical Double Layer, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy, Modeling, XPS, SEM, EDS, WLI

Surfaces and interfaces play an important role in the manufacture and/or the use of materials in various applications fields. Indeed, a material is often in contact with a solid, gas or liquid and grows within this interface different physical, chemical and electrical phenomena that are actually not well defined. More particularly, when a metal is in contact with a liquid, a charge distribution is created at the interface. This is known as the Electrical Double Layer (EDL).

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were combined in this work to determine a characteristic of the EDL, its effective capacity $\mathbf{C_{dl}}$. The chosen interface is composed by a polycrystalline Austenitic Stainless Steel 304L immersed in NaCl aqueous solution (0.01M, 0.1M, 1M). Experimental impedance diagrams are analysed using an electrical equivalent circuit (EEC) that can extract physical variables such as the electrolyte resistance $\mathbf{R_s}$ and the double layer capacitance $\mathbf{C_{dl}}$ **[1]**. The cyclic voltammetry is also used to deduce a value of the effective capacitance for various electric fields and with different voltage scan speeds **[2]**.

First investigations are focused on the development of an experimental cell and a working protocol to measure $\mathbf{C_{dl}}$. Thus, many parameters were investigated such as the influence of nitrogen flushing of the cell, the position of the counter electrode, the scan speed, the electrolyte resistance and the applied potential The results demonstrate that the double layer capacitance depends mainly on the concentration of the electrolyte and on the applied potential **(figure 1).**

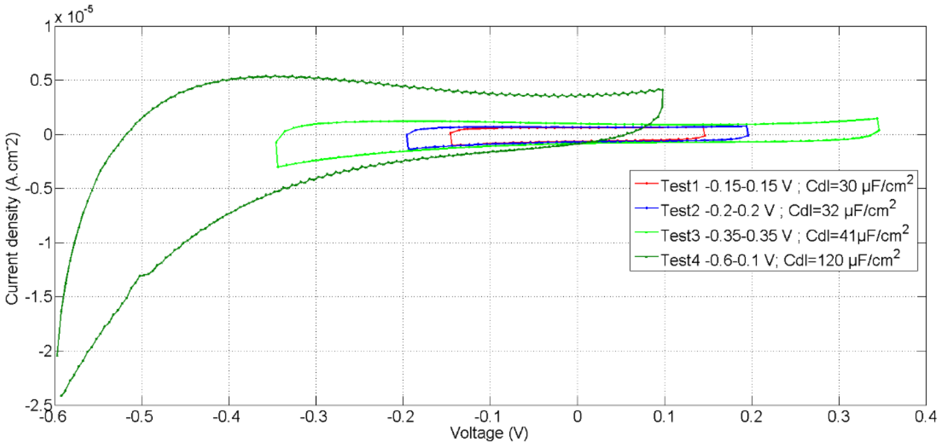

Figure 1 : Current density obtained by CV with a 304L / NaCl 0.01M solution for various intervals of applied potential ([-0.15 V ; 0.15 V], [-0.2 V ; 0.2 V], [-0.35 V ; 0.35V], [-0.6 V ; 0.1V]). The scan speed was kept at 20 mv/s. The deduced value of $\mathbf{C_{dl}}$ is indicated in the legend.

The influence on the EDL of various kinds of surface preparations (composition and/or morphology) was then studied by SIE and CV. These results were discussed in regards with physical and chemical characterisations operated by XPS, MEB, AFM and WLI.

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GCE modified with carbon nanotubes : evaluation of dispersants agents for detection of M^{2+}

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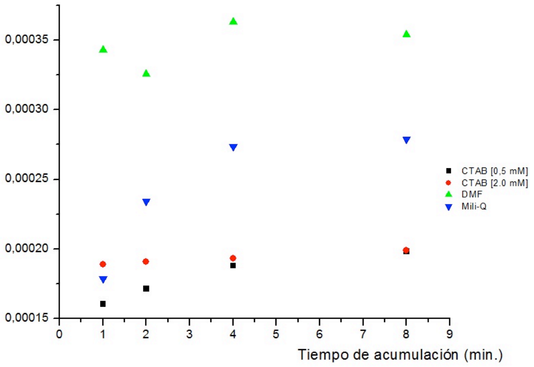
The modification of glassy carbon electrode, (GCE) with carbon nanotubes (MWCNT) for the determination of chemical species has been the subject of various investigations in recent times[1], this due to the favorable results obtained compared to using GCE unmodified , and that studies carbon nanotubes they have shown excellent conductivity due to its large area, which have an additive effect and promote an increase in the rate of electron transfer in the electrochemical reaction[2].

The aim of this work is to obtain modified electrodes that allow the detection of metal ions in solution, therefore we evaluate different dispersants agents (H_20, DMF, CTAB) to carbon nanotubes, in addition to finding the optimum parameters GCE modification, such as, concentration of the dispersion, accumulation time , reproducibility and repeatability, finally evaluate the MWCNTs / GCE in solutions of known concentration of M^{2+} (Cu and Ni), build calibration curves and measure simultaneously.



A three-electrode system was used for all measurements. A glassy carbon electrode (GCE) with a diameter of 3 mm was used as the working electrode and platinum wire as the auxiliary electrode. All measurements were carried out with an Ag/AgCl reference electrode. Electrochemical measurements were recorded on electrochemical analizer CH Instruments 620D.

MWCNTs deposition on GCE is done by taking 5 µl of MWCNT dispersion and deposited on the disc severely GCE order that MWCNTs are confined only on the active electrode area. The modification process ends after taking the GCE / MWCNT to oven for 15 min . at a temperature of 50° C , these parameters depend on the dispersing agent used.

Figure 1 shows the response of a GCE modified with 4 mg /ml of MWCNT using different dispersants, can see that for all agents used, the maximum response of intensity of current by 4 minutes accumulation time is appreciated. Although we could assume that the best dispersant is because DMF current values obtained , it is also necessary to evaluate other parameters such as repeatability and reproducibility, the latter with coefficient of variation of less than 5% where the dispersant is water used.

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Modified electrode for ozone-assisted photocatalytic degradation of phenolic compounds

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A Graphene oxide (GO) was prepared using modified Hummer`s method starting from graphite [1]. GO was impregnated on commercial nanoparticles P25 TiO_2 (GoTi). After that, reduced GOTi was obtained by hydrothermal reduction. The photocatalysis behavior of as-prepared catalyst were tested towards the phenolic compounds degradation and compared against commercial P25 TiO_2 in presence and absence of in-situ electrochemically generated ozone. The SiO_2/Ti300nm/Pt100nm/TiOx100nm/SnOx500nm electrode was used to produce ozone electrochemically. Table 1 showed that the photocatalytic degradation rate constant of phenol on RGOTi under Xe illumination in presence of H_2O_2 and electrochemically generated ozone is the better than TiO_2.

Table 1: Rate constant data in min^{-1} of phenol (20 mg L^{-1}) on Ti and RGOTi under 150 Xe illuminations in absence and absence of 70 µL H_2O_2 and Ozone

Xe		Xe + H_2O_2		Xe + O_3		Xe + H_2O_2 + O_3	
Ti	RGOTi	Ti	RGOTi	Ti	RGOTi	Ti	RGOTi
0.0214	0.0226	0.0296	0.032	0.0257	0.0262	0.0375	0.0615

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Functional Hybrid Organic-Inorganic Nanomaterials Obtained via Cathodic Electrodeposition – Application in Energy Conversion and Electrosensing

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In recent years greatly increased interest in conducting polymers, which properties can be modified by dispersed metal nanoparticle inside a polymer matrix. At the same time, their properties attributed to phenomena that can be observed with decreasing dimensionality of the material gain importance. By combining both aforementioned trends, research on organic-inorganic hybrids in the form of low-dimensional structures, for example nanowires, is developing. Nanostructured conducting polymeric materials, in particular those which properties can be adjusted by the addition of appropriate inorganic particles, are used as high-performance thermoelectric generators, magnetic memory elements, active elements of field effect transistors or solar cells, chemical and biochemical sensors and many others. The basic problem that limits practical application of nanomaterials is a relatively high cost of their manufacturing. Therefore, the research efforts are focused on the development of new, relatively easy to implement, and above all, inexpensive methods for the preparation of nanomaterials.

To obtain hybrid nanowire arrays unusually a one-step cathodic polymerization of monomer (e.g., pyrrole, Py) and co-deposition of metal ions is used [1]. A key role in the proposed synthesis method is the presence, near the working electrode, electrochemically generated nitrosyl ions, which are initiation agents for chemical polymerization of the pyrrole monomers. At the same time, a reduction of metal ions take place at the electrode. By the appropriate selection of electrodeposition potential, it is possible to obtain nanostructures consisting of polypyrrole matrix with dispersed inorganic nanoparticles.

As a result, few types of functional nanomaterials with dispersed noble metal (Ag, Pt), semimetal (Bi) and semiconductor (InSb) nanoparticles were obtained. Each of the resulting materials might find applications as i.e., sensors and electrocatalysts (PPy-Ag PPy-Pt), new materials for fuel cells (PPy-Pt) or thermoelectric energy conversion (PPy-Bi, PPy-InSb). Examples of application fields of the resulting nanomaterials are shown in Figure 1.

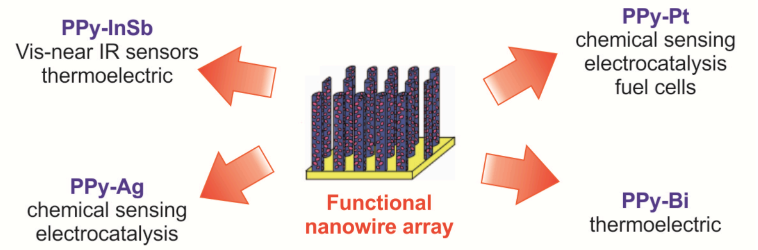

Figure 1. Possible application fields of functional hybrid organic-inorganic nanowire arrays.

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Electrochemical Exfoliation and Functionalization of Graphene Sheets

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Graphene can be prepared in large scale by the classical Hummers' method and subsequent chemical reduction. A major drawback of this widely used method is that it is a multi-steps process that requires aggressive chemicals. On the other hand, graphene sheets can be also prepared by electrochemical exfoliation of graphite.

In this work, graphene was produced by electrochemical exfoliation of graphite in aqueous electrolyte. Acidic and neutral electrolytes were used. With this procedure, graphene sheets with low oxygen content are produced. Graphene sheets were also functionalized during the electrochemical exfoliation process by using appropriate reagents and experimental conditions. The resulting materials were characterized by several techniques such as Fourier transform infrared, X-ray photoelectron and Raman spectroscopy, thermogravimetric analysis, elemental analysis, electronic conductivity measurements and electrochemical techniques.

Imaging and Electrochemical Investigation of DNA structures on HOPG Using Scanning Probe Microscopy

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Atomic force microscopy (AFM) is a very powerful technique for imaging biomolecules and entire cells under in situ physiological conditions. High-resolution images of DNA origami nanostructures can be achieved by using AFM[1]. Besides, scanning electrochemical potential microscopy (SECPM), which gives a higher resolution than AFM is another useful technique for providing structural information as well as the charge distribution information of biomolecules: e.g. we successfully used SECPM to image single enzyme molecules, such as horseradish peroxidase (HRP) under in situ conditions[2].

The DNA origami which was introduced by Rothemund in 2006[3], have received an increasing attention nowadays, because of its several potential applications, such as using it to arrange nanoparticles into a pre-designed shape, to produce label-free RNA hybridization probes, and to capture proteins. Understanding the self-assembled structures and potential dependent adsorption behavior of DNA origami on functional substrates is very useful for further design of DNA origami-based bio-sensors. In this study, we use both AFM and SECPM techniques to investigate the morphology and potential-dependent adsorption behavior of DNA scaffold and origamis on the modified HOPG surface.

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Localized studies of layered double hydroxide films grown on aluminum alloy 2024-T3

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The modification of the interface of active metal alloys through the development of chemical conversion films and application of organic coatings is one of the most used strategies to confer protection against corrosion [1, 2].

In this work we describe the synthesis and characterization of layered double hydroxide (LDH) films grown directly on the surface of 2024-T3 aluminum alloy, by a simple procedure recently reported by our group [3, 4]. The modified surface was characterized in detail by the scanning vibrating electrode technique (SVET) and the localized nature of the corrosion activity investigated. The results showed that LDH films intercalated with corrosion inhibitors act as protective layers for the aluminum substrate for long immersion times in NaCl solution, even in the presence of defects. Furthermore, corrosion rates were evaluated from SVET data and the inhibition efficiency of LDHs compared with data obtained by electrochemical impedance spectroscopy [5]. Finally, a parameter for degree of corrosion localization based upon SVET maps was introduced and could be extrapolated for the study of other systems where localized corrosion occurs.

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Glassy carbon electrode modified with gold nanoparticles and carbon nanotube/cobalt phthalocyanine film as an electrochemical sensor for diethylstilbestrol detection in water and in meat

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Diethylstilbestrol [(E)-4,4'-(1,2-diethyl-1,2-ethenediyl) bis phenol] (DES) is a non-steroidal estrogen that has been prescribed to prevent miscarriages, to combat the prostate cancer and to treat the menopause syndrome. It was also used as a growth-promoting drug for fattening livestock. However, DES belongs to the group of the emerging environmental contaminants, which are chemicals that alter the endocrine system and others deleterious effects to the human health, which allowed classify it as one of the most potential carcinogens synthetic estrogens. Although it already has been banned in several countries, such as Brazil, USA and European countries, the development of electrochemical sensors for DES detection remains relevant because DES is still illegally used in animal production to increase the animal weight. Thus, a glassy carbon electrode (GCE) modified with gold nanoparticules (AuNPTs), funcionalized multiwall carbon nanotube (*f*MWCNTs) and cobalt phtolocyanine (CoPc).was investigated as an electrochemical sensor for DES detection in water and in meat. For the electrode preparation, AuNPTs were electrodeposited on bare GCE from a plating solution containing 0.1 mol L^{-1} $NaNO_3$ and 0.001 mol L^{-1} $HAuCl_4$ and applying −0.2 V (E *vs* Ag/AgCl/Cl^{-}_{sat}) during 200 s. Next, 2 µL CoPc –MWCNTs mixture were dripped. The mixture CoPc –MWCNTs was prepared using different amounts of MWCNTs, which were previously functionalized. Cyclic voltammograms (CV) and Square Wave voltammograms (SWV) were obtained in 0.04 mol L^{-1} Britton-Robinson (BR) buffer and the solution pH was adjusted by the addition of appropriate amounts of 2.0 mol L^{-1} NaOH stock solution. Ag/AgCl/Cl^{-}_{sat}, a platinum foil (1 cm^2) and the modified electrode were the reference, the auxiliary and the working electrodes, respectively. The samples of natural water were collected from Dam Santo Anastacio, located at Fortaleza, Ceará, Brazil, while the samples of meat were acquired in a local supermarket. The water samples were stored in plastic bottles previously decontaminated with 5% HCl and maintained under refrigeration. The filtration with glass fiber filter of 0.45 micrometers was the only procedure utilized for water before the doping, with a known amount of DES. The QuEChERS method (Quick, Easy, Cheap, Effective, Rugged and Safe) method was used to extract DES from meat sample. Initially, 10g of minced meat contaminated with a known DES amount was added 20 mL acetonitrile and maintained in a ultrasonic bath for 15 min. With a vortex aid, it was added 4g $MgSO_4$, 1g NaCl and 1g of $Na_3(C_3H_5O(COO)_3)$ dehydrate and the mixture was immersed in a ultrasound bath for 30 min. After, the sample was centrifuged for 10 min at 4500 rpm. The supernatant was separated and to it was added 150 mg of primary and secondary amine exchange material (Sigma Aldrich) and $MgSO_4$ to the cleaning step. The stirring was performed manually and this resultant mixture was centrifuged for 5 minutes at 4500 rpm. The supernatant was removed and the solvent was evaporated with the aid of a rotary evaporator. Next, absolute ethanol was added to the remaining sample. All obtained DES cyclic voltammograms exhibited two oxidation peaks, about 0.26 V and 0.45 V, and one reduction peak, about -0.01 V. Furthermore, the current of anodic peaks at 0.26 V and 0.45 V obtained on CoPc-MWCNTs/AuNpts/GCE were three and five times higher than the corresponding peak obtained on bare GCE surface. The redox process was controlled by adsorption. The values of 0.675 and 1.85 were calculated for electron-transfer coefficient (β) and for electron- transfer number (n), respectively. Prior the achievements of the analytical curves, the parameters of the SWV were optimized: $f = 5\ s^{-1}$, $\alpha = 50$ mV and $\Delta E_s = 1$ mV. After, the analytical curves were obtained using a DES concentration range between 7.94×10^{-7} and 5.66×10^{-6} mol L^{-1} (R=0.9992) and the calculated detection and quantification limits were equal to 1.99×10^{-7} mol L^{-1} and the 6.64×10^{-7} mol L^{-1}, respectively. The proposed procedure was applied to determine DES concentration in water and meat in order to assess the applicability of the developed electrode. These analyses were performed for three times under the same conditions. The recoveries of DES are in the range from 94.05% to 98.56%, and indicated that the developed electrode has potential to be applied in analytical laboratory practice to determine DES in both water and meat with good sensitivity and precision.

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New Insights into Electrocatalysis of Methanol and Formic Acid Oxidation: from the Anodic vs Cathodic Peak Current Ratio Criterion to the Bifunctional Mechanism and to the Debate on the Intermediate

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A criterion frequently used in the literature to compare CO-tolerance and electrocatalytic activity among Pt-based electrocatalysts for the methanol (MeOH) electro-oxidation reaction (MOR), which originated from a paper by Manoharan and Goodenough in 1992,[1] is the ratio between the peak currents of the respective positive (anodic) and negative (cathodic) potential scans (PSs), I_f/I_b, in the cyclic voltammetry (CV) of MOR. On the other hand, there is the well-known and widely accepted Watanabe–Motoo (W-M) bifuntional mechanism proposed about four decades ago[2] for rationalizing the enhanced CO-tolerance observed for MOR on PtRu electrocatalysts. Last but certainly not least there has been an ongoing debate on the reaction intermediate therefore pathway for formic acid oxidation reaction on Pt.[3] In the presentation, we will present and discuss our most recent *in situ* attenuated-total-reflection (ATR) surface enhanced IR reflection absorption spectroscopic (SEIRAS) studies of the above three cases that have shown (1) that I_f and I_b share the same chemical origin, i.e., MOR, and the current ratio criterion is therefore an inadequate parameter to gauge CO-tolerance and catalytic activity of Pt-based electrocatalysts for MOR, thus no longer suitable for this application;[4] (2) that the long-believed poisonous CO on the Pt sites of a PtRu surface was not part of the reactions that led to the enhanced MOR activity on the latter as observed and therefore the proposed bifunctional mechanism is not the underlying process responsible for the enhanced MOR observed at low over-potential (< 0.5 V vs RHE);[5] and (3) that the reaction between the surface-bound OH group generated from water activation and the adsorbed formate as a reaction intermediate is the missing *key* link to understand FAOR on Pt and PtRu surfaces and therefore to solve the on-going debate.[6]

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New Operando Methods for Fuel Cells and Batteries: Dual-Electrode IR Spectroscopy and Stripline NMR spectroscopy

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In this presentation, we will present and discuss two new operando methods that have been developed recently in our lab for studying chemistries involved in the operation of fuel cells and batteries. The first method is the dual-electrode IR spectroscopy in which we have recently designed and built a rotating dual-electrode infrared cell for in situ electrochemical (EC) attenuated-total-reflection infrared spectroscopic (ATR-IRS) investigations of fuel cells and batteries under operating conditions. Our design is unique in that it for the first time allows for ATR-IRS measurements to be made on *both* anode and cathode while a fuel cell is operational and electrochemical measurements are on-going. We have demonstrated the device's capabilities by making sequential, iterative ATR-IRS measurements of reactions in a direct methanol fuel cell (DMFC) at the PtRu anode and Pt cathode as a function of cell driving current (thus potential) while controlling the electrochemical parameters. Different chemical species involved in the anodic methanol oxidation reaction (MOR) versus those involved in the cathodic oxygen reduction reaction (ORR) can be identified and quantified during the operation of the fuel cell. The same setup can be applied directly to study anodic and cathodic chemistry in batteries.

The second is the stripline NMR spectroscopy that is based on an electrically floating stripline detector, and is well suited to air-sensitive battery and supercapacitor research where the elements of interest are not necessarily in the liquid state. In situ NMR studies of metal-ion batteries are traditionally very challenging, and require the use of sophisticated and expensive equipment. This EC-NMR design is intended to simplify and improve in situ NMR measurements on electrodes and electrolytes of Li, Na, or other metal-ion batteries. We will present our design for the stripline EC-NMR probe and demonstrate its utility and simplicity in battery measurements. We show also the feasibility of multi-pulse experiments, which may allow for in situ imaging of the storage devices during operation. This method allows the observation and quantification of the growth of metallic microstructures (which can cause short circuits and battery failure), and can be utilized to identify conditions that promote malicious dendrite formation.

Electrochemical reactivity of biomodified solid surface

Elena Binkauskiene

Conjugated polymers is a new group of substances, whose electronic properties are close to those of metals and semiconductors. Polyaniline is one of the extensively studied conducting polymers and has been suggested for many applications (electrocatalysis, organic electrochemistry, bioelectrochemistry, sensors, energy storage, etc.) [1, 2]**.** The long-time active fungi growth within the polyaniline surface is a reliable source of modified interface [3, 4].

An exceptional combination of mycobiota/polyaniline surface interaction process seems to have great promise for change of the electrochemical, morphological and redox properties of polyaniline, which can detect unique biocomplexity and assessment of surface. The detecting of mycobiota metabolic activity on polyaniline surface is presented. For these investigations the morphological characteristics of the studied samples of polyaniline are important.

Experiments are performed under modeling condition. The polyaniline samples are exposed to Petri dishes with a pure mycobiota culture, after that the electrochemical measurements are performed. The reactivity of samples are studied by cyclic voltammetry method in the monomer-free acid electrolyte. The electrochemical analysis of the biomodified polymers completed by X-ray photoelectrons spectroscopy (XPS) and scanning electron microscopy (SEM). The SEM micrographs showed difference of topography of polyaniline treated by different mycobiota. The attachment to the polyaniline surface via the metabolic product can be indicated. This work shows significant progress in chemical research for metabolic activity definition.

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