



UNIVERSITY of the
WESTERN CAPE

3rd International Symposium on Electrochemistry

ElectrochemSA, SACI
University of the Western Cape Bellville,
SOUTH AFRICA
26-28 May 2015



New Chemical Sciences Building, UWC main campus

Scientific Committee:

Prof Priscilla Baker (Conference chairperson: University of the Western Cape)

Dr Chinwe Ikpo (University of the Western Cape)

Prof Emmanuel Iwuoha (University of the Western Cape)

Prof Kenneth Ozoemena (CSIR, Pretoria)

Dr Natasha Ross (University of the Western Cape)

Dr Vernon Somerset (CSIR, Stellenbosch)

Dr Tesfaye Waryo (University of the Western Cape)



Dear MAPET'15 delegate

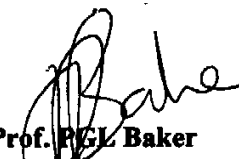
It is autumn in Cape Town and the Mother city has donned her most beautiful colours of reds and browns to welcome you to surrounds that are soft on the eye. In this beautiful setting we look forward to a stimulating scientific programme with delegates from all over South Africa and abroad. Our plenary speakers are world renowned scientists who will raise the scientific profile of the MAPET'15 international symposium to uncharted heights. Together with a diverse range of keynote lectures, invited lectures and oral presentation, MAPET'15 delegates are in for an electrochemistry revolution. So sit back and enjoy the UWC hospitality!

LOGISTICS

- Registration and the opening event on **Tuesday 26th May 2015**, will take place in the New Life Sciences auditorium. The programme will run until lunchtime, where after we will move over to the New Chemistry building for tea and poster session.
- Posters and exhibition evening will take place on level 3 and level 4 of the New Chemistry Building from 17h00-20h00, on Tuesday, 26th May 2015. Finger snacks will be served and musical entertainment will be provided by the UWC School of performing Arts.
- On Wednesday, 27th May 2015, all activities will take place in the New Chemistry building. The programme runs until lunchtime
- Buses will leave directly after morning lectures (13h00) from the New Chemistry building parking lot and take you to Neethlingshof, for lunch and (optional) wine tasting. Here you are at leisure to enjoy lunch and the beautiful scenery of the Stellenbosch wine region. Delegates will return to UWC and Hotel Verde at 16h00.
- Buses depart from UWC and Hotel Verde at 18h00 to Marimba Café, (ICC, Cape Town) where the conference banquet will take place. Buses return to UWC and Hotel Verde at 23h00.
- Invitation to contribute to the conference special issue (international peer reviewed publication) will be presented as part of the scientific programme.

Finally we wish you a pleasant stay and fruitful scientific deliberations as we welcome you at the 3rd International Symposium on Electrochemistry, themed, "*Materials Analytical and Physical Electrochemistry Today*".

Yours sincerely,



Prof. PGL Baker

Chairperson: Organising Committee MAPET'15

Chairperson: Electrochemistry Division, South African Chemical Institute (SACI)

Co-Leader: SensorLab – Chemistry department (UWC)

Materials, Analytical and Physical Electrochemistry Today



UNIVERSITY of the
WESTERN CAPE

3rd International Symposium on Electrochemistry

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26-28 May 2015



Organisers:

SensorLab, Chemistry Department, PB X17;
University of the Western Cape;
Bellville, 7535; Tel: 021 959 3051 / 3049; Fax: 021 959 1562

The organising committee of the 3rd International symposium on Electrochemistry themed *Materials, Analytical and Physical Chemistry Today* (MAPET'15) wish to gratefully acknowledge the following exhibitors and sponsors



UNIVERSITY of the
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Day I: Tuesday, 26th May 2015

Time	Activity
08h00- 09h00	Registration desk open
08h30-08h40	Welcome -Prof Swanepoel
08h40-08h55	Opening ceremony
	Energy systems
Chair:	Prof Catherine Ngila
08h55-09h00	Introduction of plenary
09h00-09h40	P1: Prof Emmanuel Iwuoha - Smart materials for novel sensor systems
09h40-10h00	IO1: Dr Remegia Modibedi - Electrodeposition of fuel cell electrocatalysts using electrochemical atomic layer deposition
10h00-10h20	IO2: Dr Christopher Arendse - Nano-crystalline silicon thin films by hydrogen profiling during hot wire chemical vapour deposition
10h20-10h40	IO3: Dr Jessica Chamier - Polymers conductors and semiconductors in photoelectrochemistry
10h40-11h00	TEA
	Energy Applications
Chair:	Prof Andrew Crouch
11h00-11h30	K1: Prof Vladimir Linkov - Overview of Research and Development in the area of sustainable energy generation and storage at South African Institute for Advanced Materials Chemistry (SAIAMC)
11h30-11h50	IO4: Dr Natasha Ross - Palladium-Gold nano-alloy modified LiMn ₂ O ₄ spinel system for enhanced Li-ion battery cathode performance.
11h50-12h10	IO5: Dr Patrick Ndungu - Lowering the operating temperature of solid oxide fuel cells using perovskite and perovskite nano-composites
12h10-12h30	IO6: Dr Bernard Bladergroen – The need for low cost utility scale batteries
12h30-14h00	LUNCH
	Electrochemical Kinetics
Chair	Prof Hailemichael Alemu
14h00-14h30	K2: Prof Jeanet Conradie - Electronic influence of different β -diketonato ligands on the electrochemical behaviour of tris(β -diketonato)M(III) complexes, M = Cr, Mn and Fe
14h30-14h50	IO7: Dr Caren Billing - Voltammetric study of bismuth(III) complexation – Overcoming the hurdles
14h50-15h20	K3: Dr Kaushik Mallick - In-situ polymerization and composite formation (IPCF): An important route for the tailoring of advanced synthetic materials
15h20-15h40	IO8: Dr Sibulelo Vilakazi - Design and development of electrochemical immunosensors for the detection of disease biomarkers
15h40-16h00	TEA
	Nanomaterials
Chair	Prof Mangaka Matoetoe
16h00-16h30	K4: Prof Andrew Crouch - Mercury analysis and methods for mercury speciation: Case studies in complex matrices
16h30-16h50	IO9: Dr P M Ejikeme - Glycerol and Ethylene Glycol Electro-Oxidation on Onion-Like Carbon-Supported Pd-MnO ₂ Nanoparticles in Alkaline Media
16h50-17h10	IO10: Dr Njomo Njagi - TaO-Mn ₂ O ₃ -Poly(4-Styrene Sulphonic acid) doped polyaniline nanocomposite materials for development of asymmetric supercapacitors
17h00	Musical Interlude – UWC Saxophone Ensemble - School of Performing Arts
19h00	Posters/ Exhibition

Day 2: Wednesday, 27th May 2015

Time	Activity
	Nanoprobes
Chair:	Prof Emmanuel Iwuoha
08h25-08h30	Introduction of plenary
08h30-09h10	P2: Prof Shiping Song - Biosensing strategies based on nanoprobes and nano-interface
09h10-09h30	IO11: Dr Philiswa Nomngongo - Application of electroanalytical techniques for determination of trace elements in environmental and fuel matrices
09h30-10h00	IO12: Dr Kevin Land - Low cost paper based diagnostics – applications and implications
10h00-10h20	IO13: Ms Suru Vivian John - Functionalization of Fullerene C60 with Novel 5-(Benzo[b]thiophene-3-yl)pyridinealdehyde Via the 1, 3-dipolar Cycloaddition Chemistry and the Investigation of the Photophysical and Electrochemical Properties
10h20-10h40	IO14: Prof Omotayo Arotiba - Poly(propylene imine) dendrimers as supramolecular architecture in electrochemical biosensor design
10h40-11h00	TEA
	Analytical
Chair:	Prof Jeanet Conradie
11h00-11h30	K5: Prof Catherine Ngila (UJ) - Nanocomposite materials for water treatment
11h30-11h50	IO15: Major Mathembi - A review of some of the bath salts identified in South African
11h50-12h10	IO16: Dr Ellen Mwenesongole - Detection of illicit drugs in waste water using GC-MS: Analytical method development
12h10-12h30	IO17: Mr M G Peleyeju - Electrochemical degradation of acid blue 40 at expanded graphite-diamond electrode
12h30-12h50	IO18: Prof Jonnalagadda - Green chemistry of ozone and scope for water treatment and value added conversions
13h00	Buses depart immediately for lunch at Neethlingshof
18h00	Buses depart for dinner
19h00	DINNER at Marimba Cafe (CTICC) Cape Town city centre

Day 3: Thursday, 28th May 2015

Time	Activity
	Biosensors
Chair:	Prof Priscilla Baker
08h25-08h30	Introduction of plenary
08h30-09h10	P3: Prof Aziz Amine - Recent advances on electrochemical biosensors based on enzyme inhibition
09h10-09h30	IO19: Dr Vernon Somerset - Nanosensing in the Aquatic Environment
09h30-10h00	IO20: Mr Fred Okumu - Electrochemical characterization of Silver-Platinum Bimetallic Nanoparticles
10h00-10h20	IO21: Dr Getrude Fomo - Aptameric recognition modulated electroactivity of poly(4-styrene sulphonic acid) doped polyaniline films for single shot detection of tetrodotoxin
10h20-10h40	IO22: Dr XG Fuku - Gallium telluride quantum dots bioelectrode system for human epidermal growth factor receptor-2 (Her2/neu) oncogene signalling
10h40-11h00	TEA

Day 3: Thursday, 28th May 2015

Environmental	
Chair:	Dr Kaushik Mallick
11h00-11h30	K6: Prof H Alemu - Investigations to Develop Electrochemical Sensors for the Determination of Phenol and Chlorophenols by Modifying Carbon Based Electrodes with Carbon Nanotubes and Poly(3,4-ethylenedioxythiophene)
11h30-11h50	IO23: Ms Diseko Boikanyo - Electrochemical Properties of Graphene and Multi-walled Carbon Nanotubes/Metal oxide nanocomposites
11h50-12h10	IO24: Prof Mangaka Matoetoe - Applications, electroactivity of nanomaterials and polyaniline composites of Ag NPs, Sawdust and Clay
12h10-12h30	IO25: Ms Omolola Fayemi - Electrochemical Detection of Phenanthrene Using Nickel Oxide Doped PANI -Nanofiber based Modified Electrodes
LUNCH	
Materials	
Chair:	Dr Vernon Somerset
14h00-14h30	K7: Prof Priscilla Baker – Actuation behavior of a derivitized pyrrole, accordion type polymer composites
14h30-14h50	IO26: Mr Neeraj Kumar - Efficient large scale synthesis of Zn-Al layered double hydroxides for enhanced adsorption of Cr (VI) and methyl orange dye effluents from water
14h50-15h10	IO27: Dr Lindiwe Khotseng - Electrode materials for direct methanol fuel cell
15h10-15h30	IO28: Mr Azeez Idris - Electrochemical detection of selenium on gold Nanoparticle modified glassy carbon electrode
15h30-15h50	IO29: Dr Francis Dejene - New materials CdS _{1-x} Te _x , Cu(In,Ga)Se ₂ , Cu ₂ ZnSn(SSe) ₄ thin films for solar energy applications
15h50-16h10	
Closing remarks	
Networking Braai	
UWC Clubhouse, main campus	

The organising committee gratefully acknowledge the support and sponsorship received from the following partners



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Materials, Analytical and Physical Electrochemistry Today (MAPET'15) THANKS YOU!!

PLENARY SPEAKERS



Prof E I Iwuoha

SensorLab, Chemistry department,
University of the Western Cape,
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Tel: 021 959 3054 email: eiwuoha@uwc.ac.za

Biosketch

Emmanuel Iwuoha is the SARChI Chair for NanoElectrochemistry and Sensor Technology at UWC and he has been a Fellow of the Royal Society of Chemistry of UK since 1999. He is a recipient of the VC's Distinguished Researcher Award for 2014 and the regional ISE award on 'Electrochemistry Excellence in Teaching and Research' in 2013. He is the Founder and Leader of SensorLab and coordinated the establishment of the first interuniversity MSc nanoscience degree programme in Africa, which involves NNMU, UF, UJ and UWC. His research interests relate to 'smart' polymeric, dendritic, graphenated and composite nanomaterials and their applications in the construction of sensors, reactors and energy generating systems (such as batteries, supercapacitors and solar cells). He has given many plenary lectures in the last 20 years, including at the 1995 Heyrovsky Discussions in Prague, the 4th World Biosensor Congress of 1996 and the 41st Convention of the South African Chemical Institute of 2013.



Basics

Name

Shiping Song

Education

BS, Biochemistry

South-Central University for Nationalities, 1995

MS, Inorganic Chemistry

Shanghai Institute of Nuclear Research, CAS, 1998

PhD, Inorganic Chemistry

Shanghai Institute of Applied Physics, CAS, 2004

Biosketch

Dr. Song obtained his PhD in Inorganic Chemistry at Shanghai Institute of Applied Physics, Chinese Academy of Sciences (CAS), in 2004. He currently holds positions as Professor in the Division of Physical Biology at Shanghai Institute of Applied Physics and Humboldt Scholar in the Institute of Inorganic Chemistry at the University of Cologne. His expertise is in the field of nanomaterials, microscale structures and biological analysis, with a special focus on the nano-based biosensors and biochips. He has received grants from the National Natural Science Foundation of China, the Ministry of Science and Technology of China, and Alexander von Humboldt Foundation. He co-authored more than 100 articles and chapters. More than 90 of his research works were published in important international journals and cited more than 3600 times. His current h-index is 30. More than 10 patents were authorized. He is an ad hoc reviewer for more than 20 international journals, as well as several granting agencies. He was a committee member of the Organic Analysis, Chinese Chemical Society. He has received several distinctions for his professional work, including CAIA Prizes of the year 2007, 2008 and 2009.

Plenary: 28th May 2015



Prof. Aziz Amine

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Biosketch

Aziz Amine is a professor of biochemistry in the Faculty of Sciences and Techniques of the University of Hassan II (Morocco). He received Ph.D. degree from the Free University of Brussels in 1993. Professor Amine's research over the last 25 years has focused on sensors and biosensors and their use in analytical chemistry. He is author of more than 100 papers in international scientific journals and an invited speaker in many International Congresses. He is a reviewer for several scientific journals and Editor of the international journal Biosensors & Bioelectronics. He was coordinator of various cooperation projects.

ORAL PRESENTATIONS

- **Plenary** -
Smart materials for novel sensor systems

E.I. Iwuoha

*SensorLab, Department of Chemistry, University of Western Cape, P. Bag X17, Bellville,
Cape Town, 7535, South Africa*

Biosensors systems constructed for the detection of disease biomarkers will be presented. They will include electrochemical sensor systems developed from biocompatible quantum dots^{1,2} and electroactive polymeric nanocomposites³⁻⁷. Some applications of the materials in disease biomarker nanobiosensors will be highlighted. As molecules or biochemical species which indicate the occurrence or severity of diseases or other physiological conditions, biomarkers and their signalling have become very essential in modern clinical diagnostic procedures and in forensic investigations. While the benefits of disease treatment are well documented, it is also important to develop diagnostic techniques for screening and for early detection of diseases. Sensor systems that will be presented are breast cancer genosensor for human epidermal growth factor receptor-2 (Her2/Neu oncogene)⁸; and coeliac disease immunosensor for anti-tissue transglutaminase antibody biomarker for gluten intolerance autoimmune disorder⁹. DNA aptamer-based estrogen disrupting affinity sensor; 17 β -estradiol receptors devised from estrogen receptor α -recombinant protein (ER- α) biosensitiser; and quantum dots genosensors for telomerase reverse transcriptase RNA cancer biomarker will be covered. Quantum dots biosensors for evaluating an individual's response profile to HIV, TB and cancer treatment drugs will be presented. The successful application of a novel plant stress signalling biomolecule¹⁰ discovered in *Arabidopsis thaliana*, in the construction of flavin monooxygenase amperometric biosensor for nitric oxide, will be discussed.

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electrodeposition of fuel cell electrocatalysts using electrochemical atomic layer deposition

Remegia M. Modibedi^{a*}, Rapelang G. Motsoeneng^b, Mkhulu K. Mathe^a, Lindiwe E. Khotseng^b, Kenneth I. Ozoemena^a

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In this presentation, electrochemical atomic layer deposition (ECALD) will be discussed as a cost effective alternative fabrication technique for fuel cell electrocatalysts towards the production of membrane electrode assemblies (MEAs). The electrocatalysts are directly electrodeposited on carbon paper thus promising good contact for MEA that maximizes catalyst utilization during cell operation. PdPt bimetallic electrocatalysts were prepared via the surface limited redox replacement reactions using copper as a sacrificial metal. The deposition sequence was alternated between Pd and Pt as the starting elements for the formation of PdPt or PtPd on carbon paper to understand the thermodynamics and kinetics of deposition. Various morphologies were observed depending on the deposition sequence. The electrocatalysts performance towards the oxygen reduction reaction (ORR) was investigated in acid electrolyte.

References

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3. R.M. Modibedi, M.K. Mathe, R.G. Motsoeneng, L.E. Khotseng, K.I. Ozoemena, E.K. Louw, Electrochimica Acta 128 (2014) 406

NANO-CRYSTALLINE SILICON THIN FILMS BY HYDROGEN-PROFILING DURING HOT-WIRE CHEMICAL VAPOUR DEPOSITION

C J Arendse, B A van Heerden, T F G Muller, F R Cummings, C J Oliphant, P H M van Loosdrecht

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The use of hydrogenated nano-crystalline silicon (nc-Si:H) thin films as the absorber intrinsic layer in silicon thin film solar cells has been extensively investigated, mainly due its improved photo-induced stability. It is well known that nc-Si:H has a distinct structural inhomogeneity in the growth direction, which results in the formation of cracks within the thin film and a reduced short-circuit current in solar cells, which eventually leads to deterioration in the solar cell performance. In this contribution, we propose a hydrogen profiling sequence, using hot-wire chemical vapour deposition, to demonstrate the deposition of a nc-Si:H thin film with crystalline uniformity in the growth direction. The dilution of silane gas in hydrogen gas (hydrogen dilution ratio) is changed from 90 to 50% at fixed time intervals to enable an investigation into the evolution of the structural properties as a function of deposition time and the eventual optical properties. Raman spectroscopy, confirmed by high resolution transmission spectroscopy, indicates crystalline uniformity in the growth direction, accompanied by the progression of an amorphous surface layer as the deposition time is increased. Infrared spectroscopy and electron energy loss spectroscopy shows low amounts of oxidation in the final deposition step. Silicon-hydrogen concentration-depth profiles, measured by time-of-flight secondary ion mass spectroscopy, confirm a graded hydrogen concentration with thickness, which is induced by the reduction in the hydrogen flow rate as the growth progresses. The optical properties were calculated by applying the effective medium approximation theory, where the existence of bulk and interfacial layers, as inferred from cross-sectional microscopy, were taken into account. The optical band gap and refractive index of the thin film grown at the initial high H-dilution are retained throughout the deposition process.

Polymers conductors and semiconductors in photoelectrochemistry

Jessica Chamier; A.M. Crouch, G.J. Summers, U.M. Waware

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Photoelectrochemical cells (PECs) extract electrical energy from light. The principle of energy conversion is the photogeneration of charge carriers (electrons and holes) upon absorption of a photon and then separation of the charge carriers to a conductive contact that will transmit the electricity. A PEC was developed for the photoelectrochemical detection of mercury (II) (Hg^{2+}). The favourable properties of a Hg^{2+} sensitive chemosensor, rhodamine 6G hydrozone derivative (RS), was combined with the semiconductor capabilities of TiO_2 to construct a sensor that is capable of generating a current in the presence of Hg^{2+} under illumination. A composite of RS and PANI was immobilized onto indium tin oxide (ITO) plates coated with TiO_2 and subjected to photovoltammetric measurements in which the optical recognition of Hg^{2+} was successfully converted to a measurable photovoltage. The Hg^{2+} -sensitive PEC had a linear photoanodic response to Hg^{2+} ranging from 10 to 200 $\mu\text{g L}^{-1}$ and a detection limit of 5 $\mu\text{g L}^{-1}$. The application of PANI is limited as it is insoluble in most organic solvents and its conductivity, energy density, catalytic activity, and electrical properties are pH dependent. Derivatization aims to increase solubility, optimise processability, and introduce recognition elements to improve the performances of sensors. Therefore there is an overwhelming interest in synthesis of copolymers of ortho- and metasubstituted PANIs that maintain the fundamental conducting backbone of PANI, while allowing for increased functionality and manageability. Copolymers of PANI, Poly(o-Bromoaniline) (P-o-BrA) and Poly(aniline-co-o-bromoaniline) (PA-co-o-BrA) with different compositions were obtained by chemical oxidative polymerization using monomer units of aniline and o-bromoaniline. The structural and functional characterization of PA-co-o-BrA copolymers was studied with UV-vis and FTIR spectroscopy. Thermogravimetric analysis showed that the bromine functionalized polymers were thermally more stable as well as soluble compared to the parent PANI. The copolymers are semi-conductive in nature, with much lower current density compared to the noble PANI, yet with comparable electron transfer capabilities. ITO and ITO/ TiO_2 coated with the P[A-co-2-BrA]s and RS had considerably lower photoresponses towards Hg^{2+} in aqueous solutions compared to PANI-RS decreasing with P-o-BrA content. Although the copolymers presented with lower photovoltages compared to PANI, their increased processability and functionalization may introduce various applications for PEC in aqueous media, especially for on-line and on-site pre-screening purposes.

Overview of Research and Development in the area of sustainable energy generation and storage at South African Institute for Advanced Materials Chemistry (SAIAMC)

V. Linkov, B. Bladergroen, S. Ji, S. Pasupathi

South African Institute for Advanced Materials Chemistry, University of the Western Cape, Bellville, South Africa

G. Swart

Alphadot Pty Ltd, Melkbosstrand, South Africa

In its pursuit for efficient low cost energy generation and storage technologies suitable for distributed power networks with maximum utilization of renewable energy sources, South African Institute for Advanced Materials Chemistry (SAIAMC) has been developing a number of technical solutions with high appeal to the market conditions of the African continent and beyond. Among those are Hydrogen Fuel Cell (HFC) generators, working both at low (up to 80 C) and medium (80-160 C) temperature ranges, Li ion batteries and Modular Battery Systems (MBS) for a KWt range power storage for commercial and residential applications and thermal sodium based batteries for utility scale energy storage and grid stabilization. Technical characteristics of newly developed fuel cells and batteries as well as systems utilizing these components will be presented in relation to their suitability for specific areas of nascent energy mix.

Palladium-Gold nano-alloy modified LiMn_2O_4 spinel system for enhanced Li-ion battery cathode performance.

Natasha Ross, Myra Nzaba, Wonderboy Ntuthuko, Chinwe Ikpo, Noluthando Mayedwa, Njagi Njomoa, Priscilla Baker, Emmanuel. Iwuoha

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Abstract: A novel transition metal alloy ($M_x = \text{Pd-Au}$) coated LiMn_2O_4 with improved high rate performances have been successfully designed and synthesized using a simple co-precipitation calcination coating approach. It is conceivably the first time that the synergistic effects of Pd-Au transition metal coating on spinel-structured LiMn_2O_4 are being explored. The surface changes effectively improved ion diffusion which led to an increase in the electrochemical reaction rate and a decrease in the cell resistance, enhancing capacity. The novel $\text{Li}[\text{PdAu}]_x\text{Mn}_{2-x}\text{O}_4$ composite has high phase purity, well crystallized particles and narrow size distributions which is suitable for lithium ion exchange. **Fig.1.** shows redox peaks residing at about 4 V corresponding to the redox reaction of $\text{Mn}^{3+}/\text{Mn}^{4+}$, while the two peaks at about 4.07 V correspond to the Li^+ exchange with the PdAu alloy. The suppressed polarization, increased peak currents and enlarged high rate capacity in the rate capability test of the $\text{Li}[\text{PdAu}]_{0.02}\text{Mn}_{1.98}\text{O}_4$ cathode were attributed to enhanced catalytic properties and reversible redox reactions in higher voltage region [1]. This suggests that the lithium intercalation and deintercalation process is much more efficient due to the increased sample conductivity and surface area. At enlarged cycling potential ranges the $\text{Li}[\text{PdAu}]_x\text{Mn}_{2-x}\text{O}_4$ sample delivered 90 mAh g^{-1} discharge capacity compared to LiMn_2O_4 (45 mAh g^{-1}). **Fig.2** shows the effective capacity of $\text{Li}[\text{PdAu}]_{0.02}\text{Mn}_{1.98}\text{O}_4$ cell declining with increased cycling, however the enduring surface conduction was significant for effective lithium intercalation and deintercalation. The cathode also showed good stability retention. The discharge pattern and performance correlates with the order of atom orientation in the structure [2]. Fig.2 inset shows the $\text{Li}[\text{PdAu}]_{0.02}\text{Mn}_{1.98}\text{O}_4$ cathode exhibited improved rate capabilities and high rate cyclic performances compared to the pristine LiMn_2O_4 . In this context, the increase in the rate of a chemical reaction due to the participation of Pd-Au catalysis shows this work significant towards the approach of developing environmentally attractive technologies. Concurrently, Pd and Au transition metal proves to be conductive and uniquely durable. This together with microscopic and spectroscopic analysis shows the Pd-Au infused- LiMn_2O_4 as an alternate superior electrochemically enhanced cathode for lithium ion batteries.

Keywords: Nanoparticles, Cathode, Electrochemistry, Batteries, Spinel LiMn_2O_4

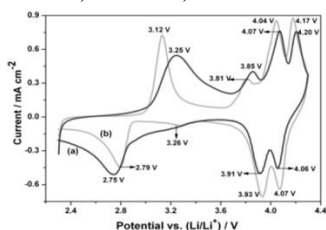


Fig.1. Cyclic voltammogram of LiMn_2O_4 (a) and $\text{Li}[\text{PdAu}]_{0.02}\text{Mn}_{1.98}\text{O}_4$ (b) in EC: DMC, 1 M LiPF_6 at 0.1 mV s^{-1}

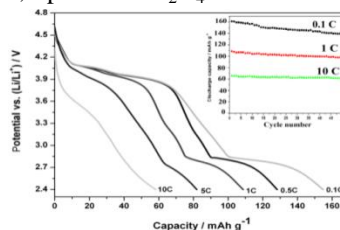


Fig.2. Discharge cycling curves of $\text{Li}[\text{PdAu}]_{0.02}\text{Mn}_{1.98}\text{O}_4$ at increasing C-rates. Inset: Cycling performance at various current rates (Charge rate: 0.1 C).

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Lowering the operating temperature of solid oxide fuel cells using perovskite and perovskite nano-composites

Patrick G. Ndungu

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Abstract

Ceramic fuel cells that operate at temperatures below 600 °C can be classified as low temperature solid oxide fuel cells (LT-SOFCs). Key drivers into research with LT-SOFCs include; they may facilitate wide scale commercialization of ceramic fuel cells, they are easier to assemble and fabricate, are highly efficient power generating systems, can utilize hydrocarbons directly, and they are fuel flexible. In terms of the materials available for developing LT-SOFCs, ceria based perovskites are the most promising to date. The current work summarizes recent efforts in the synthesis of various ceria based perovskites and nano-composites using carbon nanotubes and the perovskites. The methodologies typically use sol-gel chemistries and in some cases this was compared with chemical vapor deposition, as means to eliminate the use of excessive solvents. The physico-chemical properties of the materials will be discussed and successful tests of functional button cells operating from 300 – 500 °C will be presented.

Keywords: Low Temperature Solid Oxide Fuel Cells, Perovskites, Samarium doped Ceria, Carbon nanotubes, Iridium

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The need for low cost utility scale batteries

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The rise of global energy consumption and the environmental effects of fossil fuels derived power are forcing the diversification of energy sources to include renewable energy. Considering the intermittency of such sources and cost associated with new transmission facilities, battery energy storage proves to be a promising technology if the targets for the cost of ownership can be met.

This paper will present the cost structure of utility scale of batteries and provide a projection of various battery chemistries that can be considered. The approach for the low cost utility scale battery project at UWC will be presented as well.

- **Keynote** -
Electronic influence of different β -diketonato ligands on the electrochemical behaviour of tris(β -diketonato)M(III) complexes, M = Cr, Mn and Fe

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Classical β -diketones (1,3-substituted-propane-1,3-diones) have been known for more than a century¹ and the synthesis and properties of many metal- β -diketonato complexes are well documented, e.g. of chromium β -diketonato complexes,² manganese β -diketonato complexes³ and iron β -diketonato complexes.⁴ Metal- β -diketonato complexes have a wide range of applications in both homogeneous and heterogeneous catalysis.⁵ A fundamental knowledge and understanding of factors determining the electrochemical behaviour of β -diketones and their metal- β -diketonato complexes, could lead to the design of more efficient catalysts. A study by Kuhn *et. al.*⁶ showed that the experimental reduction potentials of a series of 10 enolized 1,3-substituted β -diketones were related to the electronic influence of the groups attached to the respective β -diketonato ligand. This contribution focuses on the electronic influence which the groups attached to the β -diketonato ligand exercise on the electrochemical behaviour (Figure 1) of a series of octahedral tris(β -diketonato)M(III) complexes, where M = Cr,⁷ Mn⁸ and Fe.⁹

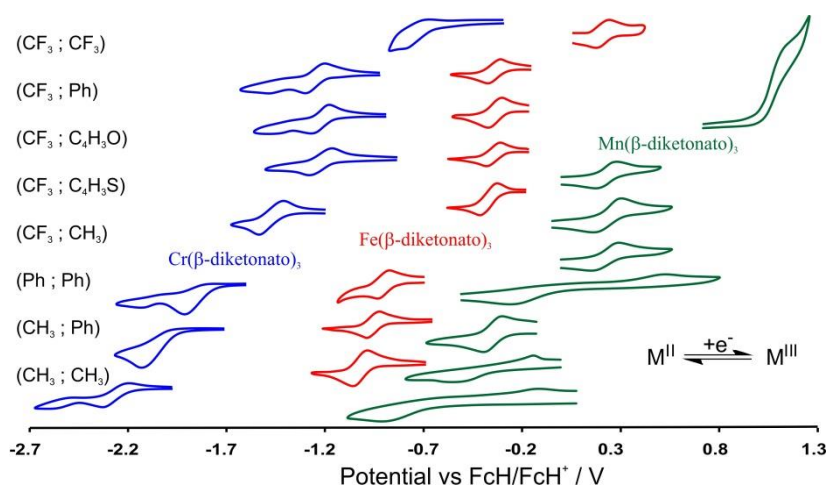


Figure 1: Comparative cyclic voltammograms of ca $0.001 \text{ mol dm}^{-3}$ of the $[\text{M}^{\text{III}}(\beta\text{-diketonato})_3]$ complexes in $\text{CH}_3\text{CN} / 0.1 \text{ mol dm}^{-3} [\text{n}(\text{Bu}_4)\text{N}][\text{PF}_6]$ on a glassy carbon-working electrode at a scan rate of 0.100 V s^{-1} . β -diketonato = $\text{RCOCHCOR}'$. Groups R and R' are indicated in the figure.

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Voltammetric study of bismuth(III) complexation – Overcoming the hurdles

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Voltammetry has been used to study metal-ligand complex formation for decades.¹ Studies were generally conducted in the same pH region as the more commonly used glass electrode potentiometry, i.e. pH 2-12. When studying aqueous Bi(III) coordination chemistry, Bi(III) hydrolyses from pH 0 and forms precipitates in the presence of supporting electrolytes at about pH 2 already.² Solution studies therefore have to commence from low pH where Bi(III) compounds are still soluble.

The benefits to employing voltammetry are that it can be used across the pH range and low Bi(III) concentrations can be used to postpone precipitation. On the other hand, the diffusion junction potential becomes significant below pH 2 and varies with pH. Since the junction potential cannot be directly measured, it was monitored by introducing into the solution a witness metal ion – one that does not undergo complexation with the ligand. Additionally the reduction potential of uncomplexed Bi(III), a critical parameter in refining stability constants, cannot be measured directly since Bi(III) is either hydrolysed or complexed by the background electrolyte anion (nitrate in this work), so procedures had to be developed to determine this value.

Bismuth coordination chemistry is not well understood (both the thermodynamic and kinetic aspects), despite its wide use of bismuth compounds in treating peptic ulcers and additional evidence indicating its possible use in the treatment of various diseases.³ This is due to the difficulties in studying this coordination chemistry. Methodologies developed to overcome the obstacles will be discussed with reference to complex formation studies of Bi(III) with various strongly binding pyridinecarboxylic acids and with the weaker binding amino acids.

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***In-situ* polymerization and composite formation (IPCF): An important route for the tailoring of advanced synthetic materials**

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Materials science is an interdisciplinary field involving the properties of matter and its applications to various areas of science and technology. With significant attention focused on nanomaterials in recent years, materials science has been propelled in a new research direction since the introduction of the nanoparticle based materials. The composites are a special class of materials originating from suitable combinations of two or more objects achieved by some appropriate technique which results unique physical properties and a wide application potential in diverse areas.

'In-situ polymerization and composite formation' (IPCF) types of reaction for the synthesis of 'metal-polymer composite material' [1] have a potential advantage in the area of 'synthetic material science' since both the polymer and the nanoparticles are produced simultaneously, which facilitates intimate contact between the particles and the polymer through functionalization [2]. Such a composite material with a higher degree of nanolevel interaction might be expected to exhibit improved performance with wider applications in various systems.

Polymer-encapsulated palladium nanoparticles have made useful contributions to synthetic organic chemistry and serve as highly active catalysts for different reactions [3-5]. Unusual transport [6] and magnetic properties [1] have been achieved at low temperature in the gold nanoparticle-polyaniline composite system, whereas individually they show normal physical properties. An extension of the IPCF approach [7] has enabled the emergence of paramagnetism within the polymer under synthesis conditions when two diamagnetic reactant species were involved. Metal nanoparticles formed during IPCF type of reactions show the efficient catalytic property for the proton coupled electron transfer (PCET) types of reactions [8].

Gold nanoparticles combined with the conjugated polymer, synthesized using an IPCF approach, form a supramolecular architecture with interesting physical properties as well as potential applications. The composite architecture shows good colorimetric and voltammetric sensor application for the detection of biomolecules where the gold nanoparticles play the role of a catalyst for both the applications in two different mechanistic pathways.

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DESIGN AND DEVELOPMENT OF ELECTROCHEMICAL IMMUNOSENSORS FOR THE DETECTION OF DISEASE BIOMARKERS

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Abstract - About 65% of deaths in Southern Africa are due to communicable diseases such as measles, cholera and others, all of which are preventable and treatable if diagnosed early. There is a need to develop sensors that are simple to use, inexpensive, that demonstrate fast response times and must further be able to withstand adverse conditions.

In this work we investigate the use of electrochemical based detection systems that can be used for the detection of communicable disease or virus biomarkers using non-invasive detection methods, using in a labeled and label-free protocols. The studied systems need to have the same sensitivity and specificity as the immunoassay based techniques however be not be laboratory centralized but be applicable to remote areas. The design and the use of impedimetric and voltammetric immunosensors will be reported. Figure 1 shows the typical protocol for measles-antibody detection using the antigen modified surface.

Keywords: Electrochemical, communicable diseases, detection.

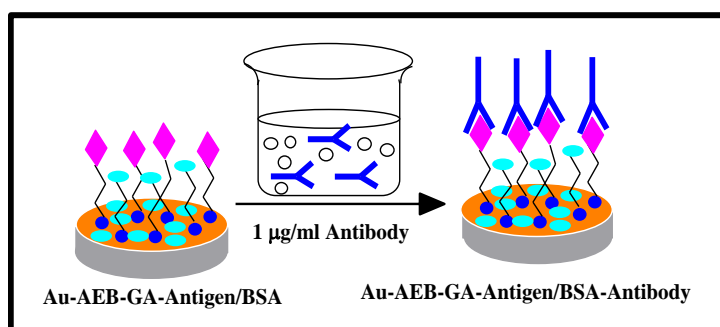


Fig. 1. **Figure 1:** Schematic representation of measles antibody detection using antigen modified surface.

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- **Keynote** -

Mercury analysis and methods for mercury speciation: Case studies in complex matrices.

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Mercury occurs naturally and as a result of human activities. One such activity is the combustion of mineral-enriched, sub-bituminous coal to produce electricity in industry that has existed for over 100 years. Although coal is absolutely necessary to supply the power that South Africa and its neighbouring countries requires, the emitted gases, especially mercury, impact the environment and present a complex array of health-related problems. Controlling the impact of mercury present in the environment depends on the efforts of governments, scientists, business and industry, agriculture, environmental organizations and individuals.

Mercury is emitted from the point sources in different forms. Accurate determination of the emitted forms or species of mercury has become a global interest. Determination of the various mercury species requires several well-understood analytical techniques for the confident assessment of potentially contaminated samples.

The presentation will give an overview of the development, validation and application of analytical methodologies that are capable of differentiating between the different forms of mercury in environmental samples (air, liquids and solids) and biological samples. Mercury sensors based on composite electrodes, photoelectrochemical sensors, Capillary electrophoresis with amperometric detection, high performance liquid chromatography with amperometric detection, and atomic fluorescence spectrometry methods were developed for mercury speciation. Very low detection limits were observed using these methods. For capillary electrophoresis with amperometric detection, the detection limits were $0.005 \pm 0.002 \mu\text{g/l}$ for Hg^{2+} and $0.4 \pm 0.05 \mu\text{g/l}$ for MeHg^+ . Detection limits of $2 \pm 0.04 \mu\text{g/l}$ and $0.01 \pm 0.02 \mu\text{g/l}$ for Hg^{2+} were observed for high performance liquid chromatography with amperometric detection and atomic fluorescence spectrometry respectively. These detection limits are attractive for the monitoring of mercury in the environment.

On application to environmental samples, very good correlations in results were observed between the different methods. Examples such as Mercury speciation in South African coal, bioavailability of mercury in biological matrices and mercury speciation in air samples will be discussed.

Glycerol and Ethylene Glycol Electro-Oxidation on Onion-Like Carbon- Supported Pd-MnO₂ Nanoparticles in Alkaline Media

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Abstract

The oxidative conversion of glycerol in electrochemical reactors is a very promising way for the generation of value added compounds from biodiesel industry waste (in its crude form, glycerol can serve as a cost effective fuel for direct glycerol fuel cells) simultaneously with either energy or hydrogen production, depending on the electrochemical reactor configuration (fuel cell or electrolysis cell, respectively) [1-3]

One pot microwave-assisted solvothermal technique was applied in the synthesis of Pd-MnO₂ nanoparticles supported on onion-like carbon (OLC), and on Vulcan carbon (XC-72) for comparison purposes. Spectral characterization of the catalysts was carried out using XRD, XPS, FESEM and HRTEM techniques. Electrochemical characterization of the novel materials was conducted in 0.5 M alcohol / 0.5 M KOH via chronoamperometric and electrochemical impedance spectroscopy as well as cyclic and linear sweep voltammetry. Generally, the catalyst supported on OLC exhibited higher current density and least charge transfer resistance relative to the catalyst supported on XC-72. The onset oxidation potential and current density of the glycerol oxidation process were 0.5386 V and 5.58 mAcm⁻², respectively. Pd-MnO₂/OLC exhibited the least charge transfer resistance and gave the best result amongst the catalyst synthesized with respect to the current density, and electrochemical stability in all the alcohols studied. The result of this effort epitomizes an important demonstration that the use of the highly graphitic carbon (OLC) as catalyst support permits the oxidation of alcohols, particularly glycerol and ethylene glycol, and could be applied in lieu of XC-72 for electro-synthesis application.

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TaO-Mn₂O₃-Poly(4-Styrene Sulphonic acid) doped polyaniline nanocomposite materials for development of asymmetric supercapacitors.

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Key words: *Sol gel method, mixed metal oxides, sulphonated polyaniline nanocomposite, electrochemical cell, supercapacitor.*

Abstract

A nanosheet poly(4-styrene sulphonic acid) and TaO-Mn₂O₃ doped polyaniline nanocomposite with electro-conductive and redox active properties was synthesized. The mixed oxide was synthesized using a modified sol-gel method and then dispersed in acidic media through sonication and entrapped *in-situ* into the polymeric matrix during the chemical polymerization of aniline doped with poly(4-styrene sulphonic acid). The oxide and polymeric composite was characterised with TEM, SEM, EDX, XRD and FTIR to ascertain elemental and phase composition, successful polymerization, doping, morphology and entrapment of the metal oxide nanoparticles. The electro-conductivity of the nanomaterial was interrogated using SECM and CV. The material was then anchored on carbon black and used in the design of an asymmetric supercapacitor cell using 2M Li₂SO₄ aqueous electrolyte. A significantly high specific capacitance value with a corresponding energy and power densities were demonstrated. The cell also showed high coulombic efficiency with a long cycle life and good cycle stability making the nanomaterial suitable for constructing supercapacitor cell electrodes.

- Plenary -:

Biosensing strategies based on nanoprobes and nano-interface

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There has been great interest in developing new nucleic acid and protein detection methods for both clinical and numerous non-clinical applications. In an effort to improve the detection ability of bioassays in our laboratory, functional nanomaterials have been actively explored to greatly enhance the sensitivity during recent years. This presentation focuses on recent progress in biosensor development by exploiting several unique optical, electronic and catalytic properties of a range of nanomaterials, such as gold nanoparticles, quantum dots, silicon nanowires, carbon nanotubes and graphene. Also, recent progress on DNA nanostructures for biosensors is provided.

The speaker will talk about how to develop nanoprobes and nano-interface with more complicated structures and more functions and how they were used to develop biosensors and biochips, either via nanoprobes that offer signal amplification, or by exploiting the inherent nanoscale effects of biomolecule-functionalized nanomaterials. All these strategies have greatly enhanced sensitivity for the detection of DNA, protein and small molecules. Some elaborately designed nanoprobes have led to extremely low detection limits down to the attomolar level, which represents sensitivity improvement up to six orders of magnitude compared to conventional detection methods.

APPLICATION OF ELECTROANALYTICAL TECHNIQUES FOR DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL AND FUEL MATRICES

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Determination of trace metal ions is very important in the context of environmental protection, food and agricultural security and high-purity materials [1]. Metals are introduced into the environment by natural and anthropogenic sources. The major man-made sources of are soils and dusts from traffic, industry and weathered materials. Therefore, there is a need to develop rapid analytical methods to monitor these pollutants. In this study, a sensitive, selective and reproducible method for quantification of mercury in waste water, gasoline and diesel samples has been developed. The procedure is based on the retention of Hg(II) in hollow fiber-supported sol-gel combined with Ambersep GT74 cation exchange resin and followed by its quantification using square wave anodic stripping voltammetry (SQWASV) at a gold nanoparticle-modified screen printed carbon electrodes (AuNPs-SPCEs). The optimization of different experimental parameters affecting the hollow fiber solid phase microextraction (HF-SPME) coupled to voltammetry, SQWASV, that is, HF-SPME-SQWASV procedure was performed using multivariate strategy. Under optimized conditions, a preconcentration factor of 854 was achieved. The repeatability (n=20) and reproducibility (n=10) expressed in terms of relative standard deviation (%RSD) were <3% and 5.3%, respectively. The limits of detection and quantification were 1.0 ng L⁻¹ and 3.0 ng L⁻¹, respectively, in the original sample. The accuracy of the developed HF-SPME-SQWASV method was tested by the analysis of spiked samples. The recovery percentages ranged from 96–100%. The proposed method was applied for quantification of Hg (II) in wastewater and commercial gasoline and diesel samples. The concentrations of Hg determined using the developed method was compared with those obtained using ICP-MS after microwave assisted digestion and the results obtained were in close agreement as statistically confirmed using Student t-test.

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Low cost paper based diagnostics – applications and implications

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Abstract:

There has been much attention paid to low cost diagnostic devices in recent years, with specific focus being placed on limited resource countries such as South Africa. In particular, there is a drive to meet the World Health Organisation's ASSURED criteria for diagnostics, namely **A**ffordable, **S**ensitive, **S**pecific, **U**ser-friendly, **R**apid and robust, **E**quipment free, and **D**eliverable to end-users.

Our group at the CSIR is actively involved in this field. An overview of the work we are focussing on to further develop paper based fluidic sensors, together with a brief overview of developments in the field, will be provided.

The flow of different media through paper, advanced printing of microfluidic flow control structures, electronics and biological material and the integration of these onto a single paper test will be presented. The importance of this technology for future health care in poorly resourced areas, together with challenges to be overcome, will be discussed. A model for distributed manufacture of the devices will be introduced, accompanied by ideas for utilising paper fluidics for education.

Functionalization of Fullerene C₆₀ with Novel 5-(Benzo[b]thiophene-3-yl)pyridinealdehyde Via the 1, 3-dipolar Cycloaddition Chemistry and the Investigation of the Photophysical and Electrochemical Properties

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A novel organic compound (5-(Benzo[b]thiophene-3-yl)pyridinealdehyde) (BTPA) with nanostructure morphology was synthesized by Suzuki coupling reaction and this was used to functionalize fullerene C₆₀ to form a solution processable fullerene derivative 3-(Benzo[b]thiophene-3-yl)-5-fulleropyrrolidinepyridine (BTFP), by utilizing the Prato-Maggini reaction [1] of 1, 3-dipolar cyclo-addition of azomethine ylides, generated *in situ* from the corresponding aldehyde and *N*-methylglycine at a temperature of 130 °C within a very short time of 25 mins. To confirm the successful synthesis of BTPA and its subsequent attachment to C₆₀, a large number of analytical techniques such NMR, MS, FTIR, TGA, UV-vis, EDS as well as HR-SEM were employed. The electrochemical and photoluminescence property of this novel material was also studied. The redox properties of BTFP, the precursor material (fullerene C₆₀) and commercially available [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) were studied by CV in dichlorobenzene/acetonitrile (4:1 v/v) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAF₆P) as electrolyte. The CV of the three fullerene materials produced three reversible redox couples corresponding to the electrochemistry of the fullerene cage. The functionalization of fullerene (i.e. as in BTFP and PCBM compounds) results in a cathodic shift in the redox peak potentials as a result of partial disruption of the conjugation of the fullerene cage [2]. The synthesised and commercial fullerenes (BTFP and PCBM) produced similar absorption bands in the UV-vis spectra, which suggests the absence of any significant difference in the band gap of both materials [3]. This also confirms the similarity in their electrochemistry. Photoluminescence (PL) quenching experiments with BTFP as acceptor, using poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) as a donor, gave 98% quenching. This means that BTFP is potentially an excellent acceptor for constructing organic photovoltaic cells.

Keywords: Fullerene C₆₀, Functionalized fullerene, Cycloaddition reaction, Suzuki coupling reaction, Photoluminescence, UV-vis, Electrochemistry

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POLY(PROPYLENE IMINE) DENDRIMER AS SUPRAMOLECULAR ARCHITECTURES IN ELECTROCHEMICAL BIOSENSORS DESIGN

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One of the philosophies of biosensing is to ensure that the reactivities, biological integrity, and bio-recognition capacity of the bioreceptor at the biosensor/analyte interface are kept as close as possible to nature – a concept known as biomimicry. To remain close to nature, the strength and types of molecular interactions that the bioreceptors are exposed to should be ‘gentle’ enough so as not to distort the bioreceptors’ structural integrity and inevitably its bio-reactivity. In nature, such ‘gentle’ interactions are usually supramolecular. Thus in the design of electrochemical DNA/aptamer/antibody/enzyme biosensors, materials and immobilisation chemistries that exploit supramolecular interactions are required. In this regard, we have applied poly(propylene imine) dendrimer (PPI) (and its nanocomposites) as supramolecular architecture in the development of electrochemical biosensors [1-3]. Dendrimers are a class of highly branched globular polymers with biocompatible properties [4]. The nanoscopic nature of PPI provides a large surface area for immobilisation and nano-wiring; the micellar nature allows host–guest encapsulation; while the cationic nature of PPI at near neutral pH lends it to electrostatic interaction with most biomolecules which are anionic at the same pH. The dendrimer platforms were prepared by electrodeposition or electro-co-deposition with gold nanoparticle on a carbon electrode by cyclic voltammetry. The immobilisation of the bioreceptor were carried out with supramolecular chemistries such as electrostatic attraction and streptavidin-biotin binding. With voltammetry and electrochemical impedance spectroscopy as the electrochemical signalling methods, we have prepared the following on PPI platforms: aptamer biosensors for HIV detection; immunosensor for cholera detection in water; enzyme biosensors for glucose, cholesterol and urea. This paper presents an overview of the PPI platform discourse and the detection of sequence – specific DNA and HIV glycoprotein 120 (gp120) based on novel generation 4 poly(propylene imine) dendrimer/streptavidin platform. In this HIV biosensor, a detection limit of 3.44×10^{-12} M (S/N = 3) and linearity $r^2 = 0.9985$ were obtained, while the aptamer biosensor detected gp120 in the nanomolar concentration range. Other biosensors based on dendrimer architecture will also be mentioned. In conclusion, our work has shown that poly(propylene imine) dendrimers are suitable nanomaterial in biosensor design.

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NANOCOMPOSITE MATERIALS FOR WATER TREATMENT

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Nanocomposite sorbents used for water treatment are functionalized conventional ceramic and polymeric membrane materials modified through various avenues. Among the numerous concepts on nanomaterial water treatment technology, the most promising to date include zeolitic and catalytic nanoparticle coated ceramic membranes, hybrid inorganic-organic nanocomposite membranes, and bio-inspired membranes such as hybrid protein-polymer biomimetic membranes, aligned nanotube membranes, and isoporous block copolymer membranes. This paper reports various approaches used to produce nanocomposite adsorbents and membranes for water purification. Selected examples include (i) synthesis of photocatalysts such as Ag, Ag₂O, ZnO, GO for degradation of organic pollutants in water; (ii) electrospinning of polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) composite functionalized by free radical grafting of acrylic acid (AA) brushes and the subsequent application for the removal of metal ions such as lead, cadmium and chromium ions from contaminated water; (iii) functionalized poly(ethersulphone) powders with carboxylic acid and amino acid groups as support for redox couples such as Fe/Pd and Fe/Ni bimetallic nanoparticles for the electrocatalytic degradation of pesticides including chlorinated compounds (dieldrin, PCB 77 and DDT) in water; (iv) Synthesis and characterization of varying composition of polyethersulfone (PES) and magnesium oxide (PES-MgO) and PES -Ag@GO nanocomposite membranes and their evaluation against bacteria. The antibacterial property of the ultrafiltration membrane was measured by the halo zone test using *E. coli*. (v) electrospinning and functionalizing of nanocatalyst loaded polyvinylidene fluoride/polyacrylonitrile (PVDF/PAN) composite (Ag/PAN/PVDF-g-PAA-TiO₂/Fe-Pd) for the dechlorination and photodegradation of pesticides (dieldrin, chlorpyrifos, diuron and fipronil); (vi) lignin, cellulose and chitosan-based nanofibers functionalized with various electron donating groups for 98% removal of metal ions as confirmed with ICP-OES. The modified functional materials have been characterized using various analytical techniques namely, FTIR, SEM, TEM, EDS, BET, TGA, XRD, CAM, among other techniques. In some of the water filtration applications, the functionalized nanofiber materials have been packed in mini-columns and employed as filters. The results have shown at least 95% removal efficiency within 10 minutes of exposure of the filters to water samples containing the target contaminants. In other cases, the nanocomposite membranes were found to be effective for the dechlorination of PCBs with reaction time of less than 30 min to attain 100% transformation. The removal efficiency of the chlorinated compounds was confirmed using gas chromatography with mass spectrometric (GCxGC-TOF-MS) detection. The sorbents have shown potential to improve the quality of drinking water. However, the challenges encountered with nanoparticle (NP) decorated membranes, include leaching out of the NPs from the nanofibers and membranes during water purification. Efforts to eliminate leaching out of nanoparticles during water purification are ongoing. Owing to their green science approach, biosorbent membranes have shown promise in water purification.

Keywords: Water treatment; Trace metals; Chlorinated organic pollutants; Bimetallic nanoparticles; Photocatalysts; Electrospun nanofibers; Nanocomposite membranes

A review of some of the bath salts identified in South African.

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Abstract:

South Africa has seen recent influx of chemical substances referred to as 'bath salts'. 'Bath salts' have no chemical relationship to any personal care product used for bathing. Bath salts sometimes referred to as 'legal highs' are designer drugs. Designer drugs are synthesized to circumvent the existing legislation and/or avoid detection through normal testing protocol. Street samples in the form of powder, tablets and capsules, submitted by the South African Police to the Forensic Science Laboratory were determined to contain benzylpiperazine (BZP); chloromethcathinone (clephedrone); Ethylone [3,4-methylenedioxy-N-ethylcathinone (MDEC, bk-MDEA)]; 4-methylmethcathinone (mephedrone), 4-methyl-N-ethylcathinone (4-MEC), methylenedioxymethcathinone (methylone), methylenedioxypropylvalerone (MDPV), N,N-diallyl-5-methoxytryptamine (5-MeO-DALT) and 5-Methoxy-N-methyl-N-isopropyltryptamine (5-MeO-MIPT). These compounds were identified using gas chromatography mass spectrometry (GC-MS). The compounds clephedrone, ethylone, mephedrone, 4-MEC, methylone and MDPV are all homologs of cathinone while 5-MeO-MIPT is a homolog of dimethyltryptamine. The compounds clephedrone, mephedrone, 4-MEC, methylone and MDPV are central nervous system stimulants, just like cathinone, and are taken to produce a cocaine- or methamphetamine-like high whilst 5-MeO-MIPT is hallucinogenic like dimethyltryptamine.

Key words: drugs chloromethcathinone (clephedrone), 4-methylmethcathinone (mephedrone), 4-methyl-N-ethylcathinone (4-MEC), methylenedioxymethcathinone (methylone), methylenedioxypropylvalerone (MDPV) and 5-Methoxy-N-methyl-N-isopropyltryptamine (5-MeO-MIPT), gas chromatography mass spectrometry (GCMS).

DETECTION OF ILLICIT DRUGS IN WASTE WATER USING GC-MS: ANALYTICAL METHOD DEVELOPMENT

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The presence of chemical pollutants in surface water has led to increasing public awareness and concern, as well as scientific interest regarding their effects on the environment. In recent years scientific interest in pharmaceutical products and illicit drugs as emerging pollutants has steadily increased. These pollutants enter the aquatic environment mainly from treated and untreated waste water discharge. In addition to being regarded as pollutants, the presence of illicit drugs in waste water has given rise to an alternative method of estimating drug usage and consumption patterns for a given population, termed as sewage epidemiology. The presence of pharmaceutical products has been well documented in waste water and emerging illicit drugs such as cathinones and piperazines are also increasingly being detected. The detection of these emerging illicit drugs in a complex matrix such as waste water, where they occur in trace levels, requires versatile, reliable, specific and sensitive analytical methods. This presentation summarizes the development of an analytical method based on solid phase extraction, derivatization with pentafluoropropionic anhydride and analysis by gas chromatography-mass spectrometry for the simultaneous analysis of 29 illicit and therapeutic drugs of abuse in waste water. Various instrumental and analytical parameters were optimised, resulting in the detection of eleven drugs of abuse including morphine, cocaine, amphetamine, methamphetamine and mephedrone in waste water from Cambridge, UK. Therefore, monitoring of waste water influent can assist in determining community drug usage as well as help inform waste water treatment processes.

ELECTROCHEMICAL APPLICATION OF EXPANDED GRAPHITE-DIAMOND MIXED CARBON ELECTRODES IN WATER TREATMENT

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In the quest for novel electrochemically robust materials for electrochemical application, we present the preparation of a mixed carbon electrode of exfoliated graphite (which exhibits good electro-catalytic property) and diamond (which possesses high oxygen evolution potential) electrodes for the electrochemical degradation of acid blue 40 dye in water. Expanded graphite (EG) and expanded graphite-diamond (EGD) composite were prepared and characterized by Raman spectroscopy, Scanning electron microscopy, x-ray diffraction and cyclic voltammetry. The EG and EGD were fabricated into electrodes and the electrodes were employed in the electrochemical oxidation of a solution of acid blue 40 in 0.1 mol dm⁻³ Na₂SO₄. The degradation process was monitored with UV-visible spectrometer by measuring the change in absorbance of the electrolyzed solution with time. Removal efficiencies of ca. 43% and 69% at EG and EGD electrodes respectively were obtained at a current density of 10 mA cm⁻² and pH 3 after 4 hours of electrolysis. The degradation kinetics of the dye follows Langmuir-Hinshelwood kinetic model. For an electrolysis time of 3 hours, the plot of $\ln(C_0/C_t)$ against time was linear. Apparent kinetic rate constants of 2.34×10^{-3} and $4.41 \times 10^{-3} \text{ min}^{-1}$ with correlation coefficient of 0.9499 0.9965 were obtained for EG and EGD respectively. The electrode preparation is simple. The diamond used in this work is the waste dust or powder obtained from the cutting of artificial diamond depicting the low cost of the electrode.

GREEN CHEMISTRY OF OZONE AND SCOPE FOR WATER TREATMENT AND VALUE ADDED CONVERSIONS

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Ozone facilitated oxidations are preferred due to the clean starting materials and reaction products. In order to improve the ozone efficiency, advanced oxidation processes (AOPs) such as O_3/H_2O_2 , O_3/OH^- and homogeneous or heterogeneous catalytic ozonation are receiving more attention as a possible treatment means for safe water and for reuse of polluted effluent. The aim of such processes was to increase the production of highly reactive species, hydroxyl radicals, through enhancement of ozone decomposition. These species may also result from the photo-catalytic processes, O_3/UV , $O_3/UV/TiO_2$ etc. which have also been applied for the degradation of many organics. Hydroxyl radicals are highly reactive, but not selective. Thereby those may react with non-target compounds and may lead to undesirable by-products.

Based on experiences of our research group, the detailed chemistry of ozone initiated oxidation processes, for oxidative degradation of organics, microbial disinfection and conversion of feed stocks to value added products will be described.

Recent advances on electrochemical biosensors based on enzyme inhibition

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Electrochemical biosensors based on enzyme inhibition represent a cost-effective, miniaturized and easy to use device for fast screening of inhibitors. They could be used as alarm systems for environmental monitoring and as a complementary technique to classical methods.

In the present conference we would like to underpin the recent advances in electrochemical biosensors based on enzyme inhibition field, focusing on:

- *the evaluation of the performances of the biosensor based on enzyme inhibition in the case of reversible and irreversible inhibition*, in terms of time of analysis, detection limit and matrix effect;
- *the use of nanomaterials* in order to improve the analytical performances of the biosensors;
- the development of biosensors based on enzyme inhibition *embedded in labs on a chip*;
- *The applications* of biosensors based on enzyme inhibition *in clinical, food and environmental samples*.

All these aspects will be critically reviewed and discussed in order to highlight the advances from 2006-2014 in this area.

Experimental results of enzymatic inhibition by pesticides aflatoxins, cyanide, sulfide, methyl-mercury, nerve agents, and various other drugs and toxins will be presented. These inhibitors were usually detected at levels of ppb. Electroanalytical applications of Carbon black as cost-effective nanomaterial in respect to carbon nanotubes will be deeply discussed. Electrodes modified with carbon black showed an enhancement of electrochemical activity.

A particular advantage of the reversible biosensors is that they offer the possibility of analysis in both batch and flow mode, allowing the use of these sensors for analysis of a large number of samples in a reasonable time interval. Irreversible biosensors, on the other hand, can be recommended for a single use with screen-printed electrodes.

Nanosensing in the Aquatic Environment

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This study is concerned with the fact that elevated concentrations of metals in the aquatic environment can be detrimental to any living organisms. Anthropogenic pollution may lead to the uptake and bioaccumulation of metals by benthic organisms, which can be transferred to higher trophic levels and pose human health risks. It is therefore important to understand and monitor the aquatic environment for the prevalence of any elevated metal concentrations to minimise the risk of pollution [1]. Studies conducted on the toxicity of platinum group metals (PGMs), its environmental bioavailability and increased concentrations in biologically relevant media have indicated that environmental exposures to PGMs may indeed pose a health risk, especially at sublevel concentrations [2-3]. Voltammetric stripping analysis is considered to be one of the most sensitive electro-analytical techniques that can be employed for the monitoring of toxic metals. This technique is very sensitive and it can be attributed to its pre-concentration step, in which trace metals are accumulated onto the working electrode surface. This is followed by a measurement step in which the metals are stripped away from the electrode during an appropriate potential scan [4-5]. In this current work the use of alternative substrates for voltammetric stripping analysis, using bismuth, antimony and silver platforms are reported from our research laboratory. In one study the construction and application of a bismuth-silver nanoparticle glassy carbon sensor for PGMs in environmental samples have shown good results. The detection limit for Pd, Pt and Rh was found to be 0.12 $\mu\text{g/L}$, 0.04 $\mu\text{g/L}$ and 0.23 $\mu\text{g/L}$, respectively with good sensitivity and reproducibility [6]. In another study the results obtained with a screen-printed carbon electrode coated with a bismuth film, have shown detection limits of 0.008 $\mu\text{g/L}$, 0.006 $\mu\text{g/L}$ and 0.005 $\mu\text{g/L}$ obtained for Pd(II), Pt(II) and Rh(III) determination, respectively [7]. These sensors have further been applied to environmental samples, showing alternatives for on-site analysis and screening of samples before tedious laboratory analysis. The results obtained for the analysis of freshwater and sediment samples are also reported.

Keywords: Platinum group metals; Stripping voltammetry; Platinum; Palladium; Rhodium; Environmental samples

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Electrochemical characterization of Silver-Platinum Bimetallic Nanoparticles

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Abstract

Metal nanoparticles have attracted a great interest in scientific research and industrial applications, owing to their unique large surface area-to-volume ratios and quantum-size effects [1]. Supported metal nanoparticles play a pivotal role in areas such as nanoelectronics, energy storage/conversion [2] and as catalysts for the sustainable production of fuels and chemicals [3]. Silver-platinum (Ag-Pt) bimetallic nanoparticles (NPs) with varying mole fractions were prepared by co-reduction of hexachloroplatinate and silver nitrate with sodium citrate. The formation of both monometallic and bimetallic NPs was confirmed via spectroscopic and microscopic techniques. Successful formation of NPs was confirmed with UV visible spectra while TEM images depicted core-shell arrangement in the bimetallic (BM) NP ratios. Detailed analysis of cyclic voltammetry (CV) gave fundamental electrochemical properties including; diffusion coefficient (D), electroactive surface coverage, electrochemical band gaps and electron transfer coefficient (α) and charge (Q). The following ranges were noted; D values (0.62-6.10 cm²/s), surface coverage (1.85-54.49 molcm⁻²), band gaps (1.45 eV-1.70 eV), transfer coefficient (0.1-0.7) and charge (0.61-17.88 C) respectively. Various trends were reported where diffusion coefficient in monometallic modified GCE was > BM GCE. Surface coverage, band gaps, transfer coefficients and charge in BM GCEs was > monometallic GCE. The electron transfer rates for the redox species at modified BM GCEs was > monometallic modified GCE with the surface redox reactions reported as adsorption controlled. The modified GCE depicts an attractive robust and advanced hybrid electrode material with great promise for development of electrochemical sensors.

Keywords: electrochemical, platinum, silver, nanoparticles, modified, electrodes, properties

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APTAMERIC RECOGNITION-MODULATED ELECTROACTIVITY OF POLY(4-STYRENESOLFONIC ACID) -DOPED POLYANILINE FILMS FOR SINGLE-SHOT DETECTION OF TETRODOTOXIN

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Tetrodotoxin (TTX) is nonpeptidic neurotoxin with a high rate of food poisoning mortality (60%) that has been associated mostly with the consumption of puffer fish based meals diets with no known anti-dote that safety concerns necessitates the deployment of analytical and detection methods compatible with points of harvest and control applications. In this paper we report the first impedimetric and amperometric electrochemical aptasensors for TTX, developed on poly(4-styrenesulfonic acid) doped polyaniline films (PANI/PSSA). The PANI/PSSA was first electrodeposited on glassy carbon electrodes (C) in its oxidized (p-doped) state (PANI⁺/PSSA) and then the amine-end functionalized TTX-binding aptamer, NH₂-AAAAATTTACACGGGTGCCTCGGCTGTCC (NH₂-Apt), was grafted via covalent glutaraldehyde (glu) crosslinking. The resulting aptasensor (C/PANI⁺/PSSA-glu-NH₂Apt) was interrogated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in sodium acetate buffer (OAcB, pH 4.8) before after incubation (30 minutes) in TTX solutions at various concentrations. Both CV and EIS showed that the binding of the analyte to the immobilized aptamer modulated the electrochemical properties, and particularly the charge transfer resistance (R_{ct}) of the PANI⁺/PSSA film, as a result of which it served as an immobilized redox probe. The analysis of the full R_{ct} vs. concentration curve (0.1 ng mL⁻¹ and 2.5 ng mL⁻¹) revealed that the interaction of adsorption of TTX followed BET adsorption isotherm with an estimated constant of BET c of 1.72 ng mL⁻¹ and a concentration of TTX adsorbed by a monolayer of 0.002 ng mL⁻¹. Based on the R_{ct} as the analytical signal, a linear response was observed in the range from 0.06 to 0.74 ng mL⁻¹ TTX with sensitivity of 226.4 Ω mL ng⁻¹ and limit of detection (LOD) of 0.12 ng mL⁻¹ using aptasensors fabricated in replicates.

Gallium telluride quantum dots bioelectrode system for human epidermal growth factor receptor-2 (Her2/neu) oncogene signalling

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Human epidermal growth factor receptor 2 (Her2/neu) is a biomarker that is overexpressed in human breast cancers. A quantum dots (QDs) based genosensor for Her2/neu oncogene was developed with gallium telluride QDs and amine-terminated probe ssDNA (NH₂-5'-AATTCCAGTGGCCATCAA-3'), that is complimentary to the DNA sequence of a section of the ERF gene of HER-2/neu (i.e. 5'-GAACATGAAGGACCGGTGGGC-3'). The QDs were highly crystalline, 6 nm in size and 3.4 eV in median band-gap. Retention of the capping agent on QDs surface was verified by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The hydrophilic nature of the capped quantum dots was confirmed by contact angle measurements, evident by contact angle of 12.2° which showed good wetting compared to that of uncapped quantum dots 79.9°. The sensor sensitivity and limit of detection values were 10.0 μA ng⁻¹ mL⁻¹ and 0.2 pg mL⁻¹ Her2/neu oncogene, respectively. Chronocoulometry (CC) and MTT assay (UV-vis spectroscopy determined the cytotoxicity of the capped QDs. Compare to literature values (5 - 62.50 μg mL⁻¹), the 3MSA capped QDs showed no cytotoxicity at this concentrations. Cytotoxicity studies using A549 human bronchial lung epithelial cells indicate that the genosensor can be customised for in vivo application.

Investigations to Develop Electrochemical Sensors for the Determination of Phenol and Chlorophenols by Modifying Carbon Based Electrodes with Carbon Nanotubes and Poly(3,4- ethylenedioxythiophene)

Prof H Alemu

Phenol and chlorophenols were investigated using glassy carbon electrodes modified with single-wall and multi-wall carbon nanotubes, and poly(3,4-ethylenedioxythiophene); and screen printed carbon electrode modified with poly(3,4-ethylenedioxythiophene)/single wall carbon nanotube composites. Voltammetric methods such as cyclic voltammetry, differential pulse voltammetry, and flow injection amperometry were used for characterizing and quantifying of phenol and chlorophenols. For the modified and unmodified electrodes, the substrate phenol has been used to characterize the electroanalytical response of each electrode. In the flow injection analysis and voltammetric measurements, optimization of experimental variables such as sequence and composition of electrode modifiers, scan rate, detection potential, flow rate, and pH of the carrier solution for the determination of phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol were performed. Under the optimized conditions, analytical parameters were calculated from the calibration curves of the measured differential pulse voltammetric, cyclic voltammetric, and amperometric responses as a function of concentrations of phenol and chlorophenols. The designed electrodes exhibited remarkable analytical performance with no need to apply pre-treatment procedure. The stabilities of the electrodes were tested by applying repetitive injections of each analyte for flow injection analysis and repetitive scans for the batch system and both showed very good operational stability. The analytical performances of the modified under flow through conditions and voltammetric system were tested and found to be impressive. The electrodes showed a wide dynamic linear range for the detection of phenol and chlorophenols as compared with other enzymatic and non-enzymatic sensors reported recently. The methods developed are quite useful for the determinations and monitoring of phenol and chlorophenols in environmental samples.

Electrochemical Properties of Graphene and Multi-walled Carbon Nanotubes/Metal oxide nanocomposites

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Graphene and multi-walled carbon nanotubes (MWCNT) have properties such as high charge mobility, electrical conductivity and high surface area which make them ideal materials for electrode fabrication. However graphene is prone to restacking which reduces its effective surface area and decreases charge transport capacity. This is remedied by modifying the graphene surface with metal oxide (MO) nanoparticles [1]. CNTs are suitable mediators for metal oxide catalyst on modified electrodes because of their good electrical conductivity and the property of being particle carriers [2]. Their excellent sensing properties towards chemical and environmental analytes have been reported [3]. Polycyclic aromatic hydrocarbons (PAH) are persistent organic pollutants which occur naturally, or from anthropogenic sources and are known carcinogens. Thus, it is important to investigate if graphene/MO is superior to MWCNTs/MO in electrochemical sensing of polycyclic aromatic hydrocarbons (PAH). Electrochemical techniques were employed for this study since they provide a rapid and cost effective way of analysing complex sample matrices. In this study, successful synthesis of graphene, acid functionalized MWCNT and metal oxide nanoparticles (NiO and Co₃O₄) was confirmed using FTIR, UV-visible, XRD, Raman spectroscopy and TEM. The electrochemical and electrocatalytic properties of graphene/metal oxide and MWCNT/metal oxide supported on glassy carbon electrode were investigated using cyclic voltammetry and electrochemical impedance spectroscopy. The electron transport properties of the carbon nanomaterial–metal oxide composite modified electrodes will be discussed. The analytical performance of the developed sensors towards PAHs detection and quantification will be compared and elucidated. The application of the developed sensor towards real sample analysis of PAHs in environmental matrices will be carried out and discussed.

Keywords: Graphene (GR), Multi-walled Carbon nanotubes (MWCNTs) Metal Oxide Nanoparticles, Poly Aromatic Hydrocarbons(PAHs), Electrocatalysis, Electrooxidation

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Applications, electroactivity of nanomaterials and polyaniline composites of Ag NPs, Sawdust and Clay

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Polyaniline (PANI), nanomaterials and polyaniline composites are commonly used in electrode modification as a means of enhancement of transduction pathways. These materials are known to improve sensitivity, selectivity, stability and reproducibility of sensor responses. Electroactivities studies of these chemical modifiers are vital in understanding their functionality. These international electrode surface changes brings about favourable interactions between analyte and the surface of the electrode by altering the thermodynamics and kinetic properties of the reactants, intermediates and products engaged in the redox changes thus widening the electrode application.^{1,2}

The core research activities are in Synthesis kinetics of Ag NPS, Pt NPS and Ag;Pt 1:1 NPs, Polyaniline composite synthesis of low cost materials(Clay, sawdust) as well as their chemical, morphological and electroactivity investigations. The application of these materials in pollution remediation and electro analysis is the major objective of the research.

The electrochemical investigations of these materials films using cyclic voltammetry were used to determine both physical and chemical properties; band gaps, surface coverage, film thickness, Diffusion coefficient. All metal NPS indicates better electrochemical properties compared to low cost materials. Ag NPs composite showed the best electrochemical activities compared to all PANIs. All parameters showed this trend Ag>PANI >CD>CL, except band gaps. All spectroscopic composites spectra's showed typical PANI characteristics with minor chemical shifts, strongly indicating Van der Waals interaction. Rods of varying sizes were observed, thus suggesting morphological dependence on HCl used and independence on type of polymerisation method and dopant.

Applications of these materials have been investigated for degradation of nitrates, extraction of PCBs, indigo dye as well as for amperometric studies (anodic stripping and square wave) of antiviral drugs: Neverapine, efavirenz and Zidovudine. Square wave analysis and immunosensor of PCBs has also been studied. The metal NPS are good for electroanalysis and degradation while the low cost composites are ideal for adsorbents.

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Electrochemical Detection of Phenanthrene Using Nickel Oxide Doped PANI - Nanofiber based Modified Electrodes

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Abstract

A nickel oxide doped polyaniline nanofiber (PANI-NiO)-based electrochemical sensor was constructed for detection of phenanthrene. The characterization of PANI-NiO was carried out using scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and ultraviolet (UV)-visible spectral studies.

The electrochemical behaviors of PANI-NiO were studied by cyclic voltammetry, square wave voltammetry and impedance spectroscopy in the presence of phenanthrene. Results showed that detection of phenanthrene was enhanced by the nanostructure of PANI-NiO film. The square wave voltammetry analysis shows a very low detection limit of 0.732 pM for phenanthrene with the linear range of 7.6 pM – 1.4 x10⁻¹¹ M. The equivalent circuit fitting of the Nyquist plots was carried out to estimate the system parameters. The reliability, stability and reproducibility of the sensor was also analyzed.

KEYWORDS: Polyaniline-nickel oxide doped nanofiber, cyclic voltammetry, glassy carbon electrode, square wave voltammetry, phenanthrene, anthracene.

- **Keynote** -

Polymer nanocomposites for measurement of polycyclic aromatic hydrocarbons in environmental samples

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PAHs are widely distributed in the atmosphere, soils, sediments and ground water as well as marine sediments. Emissions of PAHs into the air can be transported over long distances before deposition into soils, vegetation, sea or inland waters occur via atmospheric precipitation. Due to the low solubility of PAHs in aqueous media as well as their strong hydrophobic nature, these PAHs contaminants associate with particulate material in the aquatic environment with underlying sediments as their ultimate sink. High performance liquid chromatography (HPLC) is the standard method employed for the determination of the 16 priority PAHs identified by World Health Organisation (WHO). Various electrochemical methods have been used for the screening and detection of these PAHs contaminants. However, HPLC methods have a number of disadvantages associated with the method i.e. isomeric PAH peaks which partially overlap, preparation of the samples is time consuming due and matrix interferences complicate efficient measurement and quantification.

We have developed viable sensor systems for screening and quantification of the WHO priority PAHs including anthracene, naphthalene, fluoranthene, chrysene, acenaphthylene, benzo[b]fluoranthene and triphenylene. The electrochemical methods employed for the detection of these PAHs include electrochemical quartz crystal microbalance for naphthalene and fluoranthene, based on luciferase inhibition(1), voltammetric evaluation of anthracene oxidation at Ag-Au Alloy nanoparticles/overoxidized-polypyrrole composite(2) and square wave voltammetry analysis of chrysene, acenaphthylene, benzo[b]fluoranthene and triphenylene at poly(phenazine-2,3-diimino(pyrrole-2-yl) electroactive actuator. This paper will concentrate on the selectivity and specificity criteria for detection of PAHs in samples of mixed composition, towards development of a multi-array sensor ensemble for reliable and cost effective electrochemical screening method for priority polycyclic aromatic hydrocarbons.

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Efficient large scale synthesis of Zn-Al layered double hydroxides for enhanced adsorption of Cr (VI) and methyl orange dye effluents from water

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Water pollution emerged as major global environmental concern in recent years due to rapidly growing of progressive industrialization and urbanization which led the discharge of industrial effluents containing highly toxic organic and inorganic pollutants with improper treatment into water bodies. The wastewater discharged from many industries mainly consists of different types of toxic dyes and heavy metal ions. The exposure of these heavy metal ions and dyes can cause severe risks for animals and humans health due to their carcinogenesis, mutagenesis nature and toxicity. Therefore, it is essential to treat these effluents before discharge. Herein, we developed a facile and efficient route to synthesis of 2D nanosheets and hierarchical flower composed of nanosheets of zinc-aluminum layered double hydroxides (ZnAl-LDHs) on a large scale for enhanced adsorption of Cr(VI) and methyl orange dye effluents from wastewater. The influence of the molar ratio of zinc salt to aluminum salt in presence of HMTA (hexamethylenetetramine) on the morphology and structure of LDHs has been investigated. The as-prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and BET surface area, from which a possible mechanism of formation of ZnAl-LDHs is described. With relatively high specific surface area and mesopores with high diameter, ZnAl-LDHs with 2D nanosheets and hierarchical flower nanostructures were showed excellent adsorption capacity for Cr(VI) and methyl orange (MO) in wastewater. The adsorption isotherms and kinetics models were well studied. Moreover, desorption studies suggest that LDHs can be repeatedly used for the adsorption of Cr(VI) and MO. Our work proposes a new avenue to fabricate nanosheets and hierarchical flowers of ZnAl-LDHs on large scale and demonstrates that they possess excellent adsorption capabilities that could be very useful for wastewater treatment.

Electrode materials for direct methanol fuel cell

L. Khotseng, A. Bangisa

In order to achieve fine dispersion, high utilization and stable nanoscale metallic particles, catalyst-supporting material must have excellent properties including high surface area, good electron and thermal conductor among others. This study was focused on determining the best electrode material by studying carbon nanotubes which are known to have better chemical properties compared to the carbon black currently used commercially and metal oxides. The binary PtRu and PtSn catalyst currently known as best anode catalysts for direct methano fuel cell, synthesized using the polyol approach were tested with these support materials in order to make an ideal electrode. After synthesis part of the resultant electrocatalyst was heat treated to improve alloying of the secondary metal to the primary platinum metal catalyst and also to enhance the stable distribution and uniform dispersion of the nanoparticles on the support material. Physical characterization of the supported catalyst was done using XRD, HRTEM, HRSEM and EDS for elemental analysis. For electrochemical characterization RDE-CV and RDE-LSV were employed. The prepared electrocatalysts were then compared to the Pt/C, PtRu/C and PtSn/C commercial electrocatalysts accordingly.

ELECTROCHEMICAL DETECTION OF SELENIUM ON GOLD NANOPARTICLE MODIFIED GLASSY CARBON ELECTRODE

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Selenium is a trace element that is important in human diet, and in the health of plants and animals when taken in the correct amount¹. Exposures to selenium above or below the needed threshold can result in various health problems such as gastrointestinal upsets, hair loss, nerve damage, cancer to mention a few². It therefore becomes imperative to monitor the concentration of selenium in drinking water. This work presents a simple and cheaper method of detecting selenium in water using an electrochemical sensor based on gold nanoparticle (AuNPs) modified glassy carbon electrode. AuNPs was electrochemically deposited on GCE using CV within the potential range of -0.4 V to 1.1 V for 10 cycles. The modification of GCE with AuNPs resulted in an increase in the electroactive surface area of the electrode which led to the redox peak enhancement of $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ and $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox probes in comparison to the bare GCE. Square wave anodic stripping voltammetry was used to detect Se (IV) in water (in 0.1M H_2SO_4 as supporting electrolyte) at the following optimum conditions: pH 1, deposition potential of -100mV, pre-concentration time of 60 sec. The GCE-AuNP was able to detect Se (IV) to the limit of $0.64 \mu\text{gL}^{-1}$ and was not susceptible to many interfering cations except Cu (II) and Cd (II).

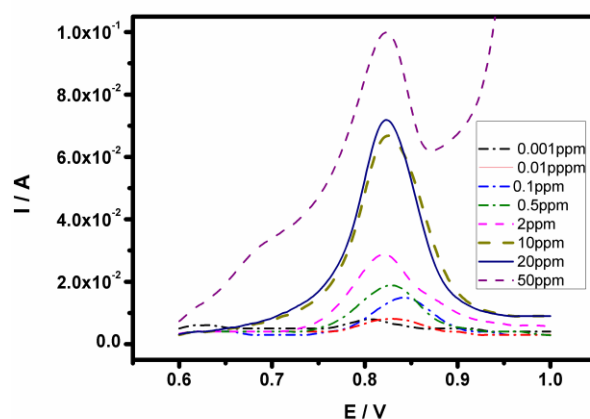


Figure 1. Square wave anodic stripping voltammetry of Se (IV) in 0.1M H_2SO_4 supporting electrolyte

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New materials $\text{CdS}_{1-x}\text{Te}_x$, $\text{Cu}(\text{In,Ga})\text{Se}_2$, $\text{Cu}_2\text{ZnSn}(\text{SSe})_4$ thin films for solar energy applications

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Abstract

The relatively small band gap values ($\sim 1\text{eV}$) of tradition solar cell materials e.g. Silicon, CuInSe_2 thin films limits the conversion efficiencies of completed $\text{CuInSe}_2/\text{CdS}/\text{ZnO}$ solar cell devices. In an effort to accelerate the development of materials-based solar energy technologies, various materials have been studied for optimum materials properties and improvement in efficiencies. In this study the $\text{CdS}_{1-x}\text{Te}_x$, $\text{Cu}(\text{In,Ga})\text{Se}_2$, $\text{Cu}_2\text{ZnSn}(\text{SSe})_4$ thin film materials for solar energy applications are deposited using various technique and investigated for possible applications. The effect of difference growth parameters are observed and correlated with the surface morphology and crystalline quality of these materials. The homogeneous incorporation of dopants into absorber layers and corresponding systematic shift in the lattice spacing parameters and band gap of the absorber films are noted and discussed.

**POSTER
PRESENTATIONS**

Determination of mercury in polluted sediments using HPLC- ICP-MS in Westbank area, Western Cape, South Africa

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A method for the determination of inorganic and organic mercury compounds in sediments was developed and validated. The method is based on the complexation of mercury compounds with cysteine and separation of the mercury species [methylmercury (MeHg), ethylmercury (EtHg) and inorganic mercury Hg (II) by HPLC. The separation was achieved on a reversed-phase C₁₈ column (15 cm x 4.6 mm id) using aqueous 0.1% w/v L-cysteine·HCl + 0.1% w/v L-cysteine mobile phase at a flow rate of 0.8 ml/min at ambient temperature. The method was found to be suitable for the routine analysis of Hg compounds in sediments as well as aqueous media and was developed to determine the influence of humic substances on the bioavailability of mercury species. The results were comparable and consistent with those determined with a Direct Mercury Analyser (DMA). The detection limit for MeHg, EtHg and Hg²⁺ were lower than 10 ng/L and recoveries for spiked samples was > 90% .

Immunosensors developed on organic clathrate transducers

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Organic noncyclic compounds were used in the development of immunosensor for rapid fish species detection. Flourene derivatives show unique chemical and physical properties because they contain a rigid planar biphenyl unit, and the facile substitution at C9 position of the flourene can improve the solubility and processability of materials containing flourene without significantly increasing of steric interactions in the compounds backbone. 9-(4-methoxyphenyl)-9H-xanthen-9-ol is bulky, rigid and has an hydroxyl moiety that may act as a hydrogen – bond donor, as well as a pyranyl oxygen which is a potential hydrogen –bond acceptor.

We have successfully synthesised 9,9'-(ethyne1,2-diyl)bis(flouren-9-ol) by reflux method and 9-(4-methoxyphenyl)-9H-xanthen-9-ol through stirring at room temperature. The products were characterised using spectroscopic methods and were found to be both UV/vis active ($\lambda_{\max} = 400$ nm flourene derivative and $\lambda_{\max} = 337$ nm xanthene derivative) and fluorescent (440nm and 467nm flourene derivative and 344 and 380 xanthene derivative). These compounds were drop coated onto commercial glassy carbon electrode (GCE) to produce thin films. Scan rate dependent cyclic voltammetry (CV) confirmed the electrodynamics of the thin films to be consistent with monolayer diffusion ($D_e = 1.37 \times 10^{-21}$ cm²/s flourene derivative and $D_e = 9.79 \times 10^{-21}$ cm²/s xanthene derivative). Surface concentration was estimated to be 1.55×10^{-13} mol cm⁻² flourene derivative and 2.00×10^{-13} mol cm⁻².

These compounds were used for the inclusion of parvalbumin antibodies immobilised onto clathrate platform by incubation and were evaluated as immunosensors for fish species identification. The antibody/antigen binding event was evaluated using UV/vis spectroscopy, electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). The immunosensor response to parvalbumin in real samples of snoek (an indigenous fish species), tuna, fish paste, eyeshadow, lipstick, omega 3&6 and scott's emulsion was evaluated. The sensitivity as calculated from EIS for each immunosensor was found to be 5.36×10^4 flourene derivative immunosensor and 4.11×10^4 xanthene derivative immunosensor and the detection limit of 1.50 pg/ml flourene derivative immunosensor and 2.42 pg/ml xanthene derivative immunosensor. The antibody/antigen binding was monitored as decrease in charge transfer resistance and increase in capacitance by EIS. The interfacial kinetics of the immunosensors were modelled as equivalent electrical circuit based on EIS data. The UV/Vis spectroscopy was used to confirm the binding of the antibody/antigen in solution by monitoring the intensity of the absorption peak.

NANOPOLYMERIC NANOBIOSENSOR PLATFORMS FOR STUDYING THE ELECTROCHEMICAL BIOTRANSFORMATION OF PAROXETINE

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Paroxetine is the second most prescribed selective serotonin reuptake inhibitor (SSRI) antidepressant drug, characterised by extensive inter-individual variation in steady state plasma concentrations which creates possibility of drug toxicity. A nanopolymeric biosensor for studying the biotransformation of paroxetine is presented. The bioelectrode system consists of cytochrome P450-2D6 enzyme encapsulated in nanotubular poly (8-anilino-1-naphthalene sulphonic acid) electrochemically deposited on gold. The biosensing procedure involved the determination of the extent of modulation of the fluvoxamine responses of the P450-2D6 enzyme electrode after incubation in paroxetine standard solutions. Paroxetine inhibited the activity of cytochrome P450-2D6 (CYP2D6) resulting in a decrease in the fluvoxamine signal of the biosensor. The biosensor gave a linear analytical response for the paroxetine in the interval 0.005 and 0.05 μM , with a detection limit of 0.002 μM and a response time of 30 s. Electrochemical Michaelis–Menten kinetics of the reversible competitive inhibition of the fluvoxamine responses of the biosensor by 0, 0.05 and 0.1 μM paroxetine, gave apparent Michaelis–Menten constant, K_M^{app} values of 1.00 μM , 1.11 μM and 1.25 μM , respectively. The corresponding, value for the maximum response, I_{MAX} was 0.02 A. The dissociation constant, K_I , value evaluated from Dixon analysis of the paroxetine modulation data was estimated to be - 0.02 μM while Cornish-Bowden analysis confirmed the competitive inhibitory characteristics of the enzyme.

DEVELOPMENT OF HYDROGEL SENSORS FOR DETECTION OF TRACE METALS OF BIOLOGICAL SIGNIFICANCE (VANADIUM AND SELENIUM)

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Selenium salts are toxic in large amounts, but trace amounts are necessary for cellular function in many organisms, including all animals, and it is an ingredient in many multi-vitamins and other dietary supplements, including infant formula. In humans, selenium is a trace element nutrient that functions as cofactor for reduction of antioxidant enzymes, such as glutathione peroxidases and certain forms of thioredoxin reductase. Recently, selenium exposure has been linked to early childhood developmental delays as well as development of diabetes type II. Vanadium is a relatively controversial dietary supplement, used primarily for increasing insulin sensitivity and body-building. Deficiencies in vanadium have been linked to reduced growth and impaired reproduction in rats and chickens. Inhalation exposures to vanadium and vanadium compounds result primarily in adverse effects on the respiratory system. Vanadium and selenium have been identified as potential human carcinogens that disrupt cellular metabolic processes at high level, causing lung cancer, brain damage and DNA damage. A fundamental understanding of metal species bioavailability and transformation in various matrices is crucial to the development of sensor and biosensor systems for monitoring trace metal loading and the role they play in biological systems.

Synthesis and Electrochemistry of Graphenated Conducting Dendritic Star Copolymer-Nanocomposite

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Graphene oxide and conducting dendritic star copolymer are fascinating materials, both scientifically and technologically, due to their exceptional properties and their potential in applications ranging from high-frequency electronics to energy storage devices. The development of an active electrode material with high capacity of performance is indispensable for energy storage applications. A new nanocomposite conducting star-complex macromolecular architecture having graphenated conducting dendritic star copolymer-nanocomposite has been successfully chemically synthesized via *in situ* polymerization of dendritic star copolymer on graphene oxide (GO). The synthesis procedure involves a condensation reaction between the diamino functional polypropylene imine dendrimer (PPI) and 2-pyrrole aldehyde to produce the pyrrole functionalized PPI dendrimer. Chemical oxidative polymerization of the pyrrole functionalized PPI dendrimer (PPI-2Py) with additional pyrrole monomer and graphene oxide give graphenated-poly(propylene imine)-co-polypyrrole (GO-PPI-co-PPy). The formation of composite was analysed using electrochemistry, X-ray diffraction, Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). However, thermal stability of the PPI dendrimer interior was improved dramatically as a result of graphenated copolymer formation. Scanning electron (SEM) and transmission electron microscopy (TEM) clearly show sheet-like layered structure of graphene oxide surrounded by star copolymer. The impedimetric studies showing that the composites can be used as electrode material for supercapacitor applications.

Designing next generation high energy density lithium-ion battery with manganese orthosilicate-capped alumina nanofilm

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The development of clean and renewable energy technologies clearly emphasizes the need for high energy density batteries. Lithium metal orthosilicates attract great attention as high capacity cathodes for new generation Li-ion batteries due to the possibility of exchanging more than one Li-ion per redox-active transition metal ion [1]. The electrochemical performance of lithium manganese orthosilicate ($\text{Li}_2\text{MnSiO}_4$), with a superior theoretical capacity of 333 mAhg^{-1} upon complete delithiation, is limited by low intrinsic electronic conductivity, thus affecting its practical application [2]. This research will present a combination of hydrothermal and sol-gel synthetic routes to produce nanostructures of $\text{Li}_2\text{MnSiO}_4$ and further coating with a thin film of aluminium oxide in order to reduce the diffusion pathway of Li-ions as well as to enhance its electronic conductivity. Results from High-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) for morphological, crystallographic and functional group analysis will also be presented. Electrochemical studies were performed using Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) to investigate lithium ion intercalation dynamics and kinetics, reversibility of electrode reactions and the determination of the charge transfer resistance (R_{ct}) and the Warburg impedance respectively.

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Polyacrylic acid and polyvinylpyrrolidone stabilised ternary nanoalloys of platinum group metals for electrochemical production of hydrogen from ammonia

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For years, South Africa has been facing an increase in energy demand. Hydrogen fuel cells have been considered as future energy alternatives. Even though hydrogen could be generated via various chemical reactions, ammonia gas is one of the feedstock for the production of hydrogen. The electro-catalytic oxidation of ammonia is slow and surface sensitive. Consequently catalysts are required to facilitate the reaction. Owing to their unique catalytic properties, nanoalloys of platinum group metals (PGMs) are being designated as possible electrocatalysts for ammonia oxidation. This study will involve the chemical synthesis of unsupported ternary PGMs nanoalloys such as Cu-Pt-Ir and Fe-Pd-Ir. The nanoalloys will be stabilized with poly (acrylic acid sodium salt) (SPA) or polyvinylpyrrolidone (PVP) capping agent. The structural properties of the nanoalloy systems will be determined by using UV-Visible (UV-Vis), solid state Nuclear Magnetic Resonance (NMR), Fourier Transform Infra-Red (FTIR), Surface Enhanced Raman (SER) and X-Ray Diffraction (XRD) spectroscopic techniques. The elemental composition and particle size of the materials will be evaluated by High Resolution Transmission Electron Microscopy (HRTEM) coupled to Energy Dispersive X-ray (EDX) spectroscopy. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) will be used for morphological characterisation. The electrochemistry of the nanoalloy materials will be interrogated with Cyclic Voltammetry (CV), Square Wave Voltammetry (SWV) and Electrochemical Impedance Spectroscopy (EIS). Platinum electrode will be modified with the nanoalloys for application as electrocatalyst for the oxidation of ammonia. The electrochemical parameters such as formal potential for optimal electrocatalysis, the effect of pH, the turnover rate of the PGM nanoalloy electrocatalysts will be evaluated.

Keywords: Platinum group metal alloys, fuel cells, ammonia electro-oxidation, nanomaterials.

**Dendritic Nanocomposite of Naphthalene Diimide and
Poly(propylene thiophenimine)-co-poly(ethylenedioxythiophene)
for Possible Applications in Organic Photovoltaic Cells**

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Solar energy is produced as a result of the absorption of photons by a semiconducting material; inducing electrons to be ejected and taken up by the electric field to produce charges. In a solar panel the semiconducting material is sandwiched between two electrodes, this component is what is known as a cell. Within the field, organic bulk heterojunction photovoltaic cells have proved of being able to have a great impact in the future years; mainly due to easy processability, cost effectiveness and above all, a good power conversion efficiency associated to the close 3-dimensional interpenetrating network that is generated from blending donor and acceptor semiconducting materials together in a bulk heterojunction active layer. This research work is a report on the study of a newly developed organic bulk heterojunction active layer based on a blend of a star-copolymer generation 1 poly(propylenethiophenimine)-co-poly(ethylenedioxythiophene) (G1PPT-co-PEDOT); the donor material with N,N-diisopropyl naphthalene diimide (NDI) as acceptor material. Both materials were chemically synthesized. The synthesis of G1PPT-co-PEDOT involved the functionalization of generation 1 poly(propyleneimine) tetramine, G1PPI into G1PPT by condensation reaction, followed by the copolymerization of G1PPT with ethylene dioxythiophene (EDOT) monomer. NDI was also synthesized via condensation reaction. Both materials were characterized using spectroscopic, voltammetric and microscopic techniques. Based on the voltammetric and spectroscopic results, the HOMO, LUMO and band gap energy values of both the donor and acceptor were calculated to be -4.03 eV, -6.287 eV and 2.25 eV for the donor respectively and -4.302 eV, -7.572 eV and 3.27 eV for the acceptor respectively. From these results, the energy diagram was drawn and revealing that the separation between the HOMO of the donor and the LUMO of the acceptor $\Delta E_g = 1.985$ eV.

Polyanilino-Graphene Oxide Intercalated with Platinum Group Metal Nanocomposites, for Application as Novel Supercapacitor Materials

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Supercapacitors are one of the important subjects concerning energy storage which has proven to be a challenge in this country. Currently, the electrodes of most commercial supercapacitors are made of carbon which is known to be inexpensive and has high resistance to corrosion. These carbon based supercapacitors operate under EDLC. They offer fast charging/discharging rates and have the ability to sustain millions of cycles without degrading. With their high power densities, they bridge the gap between batteries which offer high energy densities but are slow in charging/discharging and conventional dielectric capacitors which are very fast but having very low energy densities. The objective of this work was to develop a high performance supercapacitor using polyanilino-graphene oxide intercalated with platinum group metal nanocomposites. Specific capacitance of each material was investigated with the objective of ascertaining the material that has the best capacitance. In this work, GO was functionalized with aniline and intercalated with Pt, Pd and Pd-Pt nanocomposites. The nanomaterials were characterized with FTIR, Ultraviolet-visible (UV-visible) spectroscopy, high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), energy dispersive x-ray microanalysis (EDS) and X-ray diffraction (XRD) analysis. The composites were tested for possible application as supercapacitor materials using potentiostatic-galvanostatic constant current charge/discharge. The synthesized materials had good electronic, mechanical, optical, physical etc. properties as proven by the various characterization techniques but they proved not to be ideal for application as supercapacitor materials. The materials tested negative when tested for both anodic and cathodic materials therefore we can conclude that the materials are not good supercapacitor materials and therefore cannot be used in application as novel as supercapacitors.

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Polyamic acid/Graphene Oxide Composite for Electrochemical Screening of Antibiotic Residues in Water

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Antibiotics are very useful pharmaceuticals which are used to treat infectious diseases on humans and animals. Antibiotics can be more or less extensively metabolized by humans and animals. After administration, antibiotics for human use or their metabolites are excreted into the effluent and reach the sewage treatment plant (STP). Not all Antibiotics in sewage treatment plants are eliminated. This can lead them to pass through the sewage system and may end up in the environment, mainly in the water compartment. Residual amounts of these antibiotics can reach surface waters, groundwater or sediments. These antibiotics in water may lead to induction and spread of harmful bacterial resistance which may be harmful to humans or animals. Electrochemical based sensors and biosensors have emerged with advantages of being simple, uniform whole structures featuring direct transduction, high bioselectivity, high sensitivity, miniaturization electrical/ optoelectronic readout, continuous monitoring, ease of use, and cost effectiveness. The development of composites based on conductive phases dispersed in polymeric matrices has led to important advances in analytical electrochemistry, particularly in electrochemical sensor devices. In this study polyamic acid - graphene oxide composites will be prepared for electrochemical screening of environmental pollutants in wastewater. Polyamic acid and graphene oxide will be synthesized independently; will be characterized using cyclic voltammetry (CV), square wave voltammetry (SWV), electrochemical impedance spectroscopy (EIS), atomic force microscopy (AFM) and Scanning electron Microscopy (SEM). Three different ratios of the polyamic acid –graphene oxide composites (20 : 80 ,50 : 50 and 80 : 20) will be prepared and characterized with CV ,SWV ,EIS ,FTIR and SEM. The prepared composites will be then applied to antibiotic residues including Norflaxacin, Neomycin and Penicillin G. Cyclic Voltammetry , Square wave voltammetry (SWV) and electrochemical impedance spectroscopy are the techniques which will be used to measure electrochemical signals of the analytes. The aim of this study is to determine which ratio of the polyamic acid –graphene oxide composites shows high sensitivity and selectivity in the detection of each specific antibiotic residues hydrocarbons in wastewater.

Cytochrome P450-3A4/Copper-Poly(propylene imine)-Polypyrrole Star Copolymer Nanobiosensor System for Delavirdine – A Non-Nucleoside Reverse Transcriptase Inhibitor HIV Drug

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In this project a nanobiosensor system was devised and used for the determination of the metabolism of delavirdine, a non nucleoside reverse transcriptase inhibitor (NNRTI) ARV drug. The nanobiosensor was prepared by the entrapment of the isoenzyme CYP3A4 into a pre-formed electro active carrier matrix consisting of a dendrimeric copper generation-2 poly(propylene imine)-co-polypyrrole star copolymer (Cu(G2PPI)-co-PPy). The metallo-dendrimer was used as a host for the enzyme and provided the necessary bio-compatible environment that allowed the direct transfer of electrons between the enzyme's active centres and platinum electrode surface. Cu(G2PPI)-co-PPy was prepared by the incorporation of the copper metal into the G2PPI and the electropolymerization of pyrrole onto the Cu(G2PPI). The incorporation of Cu into G2PPI was determined by FTIR which did not show the presence of the Cu but showed an increase in the intensities of the peaks after the incorporation. The surface morphology of Cu(G2PPI) was confirmed by the use of HRSEM which showed a difference in the surface morphology of the dendrimer moiety with the addition of the copper metal. The HRSEM images after Cu incorporation resulted in the change from rough surface to smooth surface with open cavities which were essential for the entrapment of the biological systems (CYP3A4). Energy dispersive spectrometry (EDS) and HRTEM were used to confirm the presence of spherically shaped copper nanoparticles in the Cu(G2PPI) and were found to have a size distribution of 12-17 nm with an average particle size of 15 nm. The star copolymer (Cu(G2PPI)-co-PPy) was characterised using cyclic voltammetry where it was confirmed that the material was electroactive and conducting due to electron movement along the polymer chain. A diffusion co-efficient (D_0) value of $8.64 \times 10^{-5} \text{ cm}^2/\text{s}$ was determined for the material indicating a slow electron transfer kinetics within the diffusion layer. The resultant nanobiosensor parameters include a dynamic linear range (DLR) of 0.01-0.06 nM, a limit of detection (LOD) of 0.025 nM and a sensitivity value of $0.379 \mu\text{A}/\text{nM}$.

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Graphene amplification of the sensitivity of polyaniline-tungsten oxide electrochemical sensor for Pyrene

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A graphenated glassy carbon electrode (GCE) was doped with polyaniline-tungsten oxide nanoparticles (PANI/WO₃) by electropolymerization of a mixture of aniline and tungsten oxide on a graphene (GR)-modified GCE. The novel PANI/WO₃/GR/GCE nanocomposite electrode system that was formed was characterized and tested as a sensor for pyrene, a polyaromatic hydrocarbon (PAH).

The electrode was found to be effective in the electro-catalytic oxidation of pyrene only when it contained graphene. The values of the calibration parameters of PANI/WO₃/GR/GCE when applied as a pyrene sensor, were 1.0 - 10.0 pM and 0.132 pM for the dynamic linear range (DLR) and the limit of detection (LOD), respectively. The analytical importance of the sensor is the fact that its LOD and DLR values are by at least 3 orders of magnitude lower than the WHO permissible level of 1.12 nM pyrene in wastewater.

APTAMER NANOBIOSENSOR ASSAY FOR ESTROGENOUS ENDOCRINE DISRUPTING CHEMICALS IN TREATED WASTEWATER

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Environmental chemicals that disrupt normal endocrine functions in living organisms including humans, are of great concern globally. These chemicals as a group are known as endocrine disrupting compounds (EDCs). EDCs may imitate modulate and block hormone synthesis. Estrogenic compounds that are present in the environment above a certain concentration (threshold limit value), are known to have adverse effects on health and reproductive patterns in wildlife species. Analytical and biological detection methods currently utilised, are time consuming, costly and require highly skilled operators. Electrochemical sensors and biosensors are well established in literature as simple and sensitive technology for a wide range of environmental analysis. We have developed a highly responsive aptamer-immuno electrochemical protocol which is inexpensive and easy to implement. An objective of this study is to develop an aptamer-immuno sensor for rapid, highly specific and simultaneous determination of low levels of EDCs in treated wastewater. We report an aptamer-immunosensor assay for 17-betaestradiol developed using poly (2, 5 dimethoxyaniline) doped with polyvinyl sulfonic acid (PVSA) in the presence of Zinc Oxide nanoparticle, coated on glassy carbon electrode. The undoped poly (2, 5 DMA) and doped PVSA will be prepared in hydrochloric acid respectively by electrochemical oxidative polymerisation and the polymer will be investigated in detail electrochemically and spectroelectrochemically. Electrodeposited or coated films will be studied as multifunctional platforms for immobilizing biorecognition agents (antibody, aptamer) to achieve selective electrochemical aptamer-immunosensor for 17-betaestradiol. The platform and the aptamer-immunosensor will be interrogated by voltammetry and impedimetry and applied in real water samples. The results will be compared with conventional analytical methods based on high pressure liquid chromatography (HPLC) and enzyme linked immunosorbent assay (ELISA) techniques.

Palladium telluride quantum dots and cytochrome P450 biosensor for the detection of breast cancer drug – tamoxifen

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Tamoxifen is an oral non-steroidal anti-estrogen drug used in the prevention and treatment of all stages of breast cancer. This drug acts by competing with estrogen for binding to the estrogen receptor (ER) and reduces the transcription of estrogen dependent genes. However, approximately 30-50% of ER-positive breast cancer patients either fail to respond or eventually become resistant to tamoxifen resulting in a serious clinical challenge in breast cancer management. This, therefore, calls for new selective and sensitive methods for evaluating individual's metabolic activities of the drug ensuring in this way reliable dosing of the drug. This poster presents a biosensor system based on the combination of thioglycolic acid-capped palladium telluride (TGA-PdTe) quantum dots (QDs) and cytochrome P450-3A4 or 2D6 (CYP3A4 or CYP2D6) enzymes for the determination of tamoxifen. Preliminary FTIR and UVs studies of the QDs confirmed the presence of the capping agent via the specific COOH and CH₂ signature bands; furthermore the adsorption band at ca. 330 nm and the corresponding band gap energy, E_g , value is 3.47 eV (within the E_g value for QDs particles) confirmed the successful synthesis of the TGA-PdTe QDs. Differential pulse voltammetric (DPV) electroanalysis using the Au|Cyst|TGA-PdTeQDs|CYP3A4 (or CYP2D6) biosensor systems indicated a clear catalytic cathodic peak at -0.35 V for the tamoxifen biotransformation reaction; this signal was used, in this work, as the biosensor analytical response. The developed biosensor presented a limit of detection (LOD) of 0.98 and 2.5 ng/mL, for CYP3A4 and CYP2D6 based biosensors, respectively. These are lower than tamoxifen's maximum steady state plasma concentration (C_{max} 40 ng/L) value; these performances make the proposed biosensor a promising platform for monitoring the drug in patients.

Evaluation of electrochemical performance of transducers as rapid response sensors

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Antibiotics are defined as any class of organic molecule that kills or inhibits microbes by specific interactions with bacterial targets. Antibiotics may be classified based on bacterial spectrum (broad versus narrow), route of administration, type of activity (bactericidal versus bacteriostatic), and origin (natural versus synthesized), and can also be classified based on their chemical structure. The intensive use of antibiotics for human (domestic and hospital use), veterinary and agriculture purposes, these compounds are continuously released into the environment from anthropogenic sources, such as wastewater treatment plants which are considered as one of the major source of evolution and spreading of antibiotic resistance into the environment. In this study chemical sensors based on polymer nanocomposites will be developed for the detection of antibiotic residues. Three antibiotics (Norfloxacin, Penicillin and Neomycin) will be detected. Chemical sensors prepared from novel homogeneously blended polysulfone and graphene oxide suspensions, will be characterised using the cyclic voltammetry (CV), square wave voltammetry (SWV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS) to determine formal potential, diffusional and interfacial charge transfer properties. Ultraviolet-visible spectroscopy (UV-Vis), fourier-transform infrared (FTIR) and scanning electron microscopy (SEM) will be used to evaluate charge transfer phenomenon and surface morphology. The qualitative analytical performance of the polymer nanocomposite sensors towards the selected antibiotic residues, will be reported on.

ELECTROCHROMISM IN ELECTRODEPOSITED POLYAMIC THIN FILMS

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PLC. olyamic acid (PAA) was chemically synthesized from two starting materials, ODA and PMDA using acetonitrile as solvent. The chemically synthesized product was characterized using FTIR spectroscopy and UV/vis spectroscopy. PAA was drop coated onto GCE and electrodeposited onto ITO electrode and characterized using electrochemical methods (cyclic voltammetry, square wave voltammetry), UV/vis and UV/vis Spectro-electrochemistry. The morphology of the prepared electrodes was studied using scanning electron microscopy (SEM). The electrodeposited PAA thin films were observed to have two redox couples with a formal of 266 mV and -283 mV (vs Ag/AgCl). The diffusion coefficient (D_e) determined from cyclic voltammetry was found to be 7.9×10^{-6} cm²/s and provide a measure of how fast charge is transported through the thin film. PAA showed a broad absorption peak at 214 nm due to the carbonyl chromophores within the polymer and shoulder peak at 293 nm from a quinoid-type chromophore. The calculated band gap of 4.23 eV indicated the polymer was optically transparent. Spectro-electrochemistry measurements were performed on the PAA thin films while applying a fixed potential, to evaluate electrochromic properties of the polymer. The polymer itself showed no electrochromic shift, but a decrease in absorbance was observed, as a function of applied potential. PAA was found to be optically transparent between 300 and 800 nm throughout all experiments. The analytical response of anthracene and naphthalene was studied at the ITO/PAA using spectro-electrochemistry. The characteristic analytical absorbance signal for anthracene was clearly identified at 375 nm when ITO/PAA electrode was polarised at -800 mV (vs Ag/AgCl). The calibration curve for anthracene showed a linear response from 4.95×10^{-4} M to 1.15×10^{-2} M. The analytical absorbance signal for naphthalene was observed at 225 nm was superimposed on the background absorbance of ITO itself. The calibration curve for naphthalene showed a linear response from 5.66×10^{-3} M to 1.07×10^{-2} M. The ITO/PAA showed a low detection limit and high sensitivity for anthracene and naphthalene, making it a suitable platform for spectro-electrochemical analysis of PAHs. The limit of detection was found to be comparable with other previously used methods, HP

Key words: Electrochromism, spectro-electrochemistry, polyamic acid, UV/Vis spectroscopy, optical transparent

Bimetallic Electrochemical Sensor based on the nanocomposite of rGO-SbNPs for the detection of platinum group metals

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Along with the progress in the industrial and technological fields, pollution has been one of the main concerns across the world. Its impact on the environment has led to the development of different approaches to detect, prevent, or minimize its damaging effects. Heavy metals are among the most important soil, water and biological contaminants. Electrochemistry is likely to cope with this high demand by offering new types of electrodes for real-time detection of various metallic contaminants in environmental samples and also in biological and biomedical samples. In electrochemical processes, electron transfer across the solid-liquid interface is the elementary step and the interfacial properties such as conductivity, surface area, etc. have significant influence on electron transfer. Therefore, preparation of well-defined electrochemical interface with highly controllable properties is significant for both the fundamental and the applied studies in electrochemistry. Nanoparticles of noble metals were utilised by electrochemists to modify the surface of conventional electrodes to obtain better electrochemical responses due to larger effective surface area, increased mass transport, and better electronic interaction between the analyte and the electrode [1-3]. For the purpose of this work, bimetallic nanoparticles were applied for designing novel sensing systems, which lead to higher catalytic activity, enhancing the performance and improving better sensitivity and selectivity occurring on sensing surfaces. This work focuses on the nanocomposite based on synthesis of reduced graphene oxide and antimony nanoparticles. The obtained nanocomposites were modified on a carbon electrode surface and employed in stripping voltammetry for the detection of platinum group metals in 0.2 M NaOAc buffer solution. Several operational parameters were optimised to enhance the electroanalytical performance of the modified glassy carbon electrode. The results presents sharp stripping peaks and a relatively constant peak potential with a good linear behaviour in the examined concentration range from 40 to 400 pg.L^{-1} for all precious metal ions. The detection limit was found to be 0.45, 0.49 and 0.49 pg.L^{-1} for Pd(II), Pt(II) and Rh(III), respectively, which is below the WHO guidelines for freshwater.

Keywords: Bimetallic, Electrochemical sensor, Environmental samples, stripping voltammetry.

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Application of a bismuth-silver bimetallic nanosensor for the voltammetric analysis of platinum group metals in environmental samples

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Nowadays, the pollution of surface waters with chemical contaminants is one of the most crucial environmental problems. These chemical contaminants enter rivers and streams resulting in tremendous amount of destruction to the aquatic ecosystem [1]. Heavy and platinum group metal (PGM) contaminations at trace levels in water resources presents a major environmental threat, so the detection and monitoring of these metal contaminants results in an ever-increasing demand [2,3]. According to El Mhammedi *et al.* (2009) [4], heavy metal analysis has been performed in laboratories with time-consuming sampling, transportation and storage steps. Spectroscopy instrumentation was used for the simultaneous analysis of metal ions in water, sediment and biota samples. For the detection of trace metals electrochemical analysis has always been recognized as a powerful tool. This study dealt with the development of a bismuth-silver bimetallic nanosensor for differential pulse adsorptive stripping voltammetry (DPAdSV) of PGMs in environmental samples. The nanosensor was fabricated by drop coating a thin bismuth-silver bimetallic film onto the active area of the SPCEs. Optimisation parameters such as pH, dimethylglyoxime (DMG) concentration, deposition potential and deposition time, stability and interferences were also studied. In 0.2 M acetate buffer (pH = 4.7) solution and DMG as the chelating agent, the reduction signal for PGMs ranged from 0.2 to 1.0 ng L⁻¹. The detection limit for Pd(II), Pt(II) and Rh(III) was found to be 0.07 ng L⁻¹, 0.06 ng L⁻¹ and 0.2 ng L⁻¹, respectively. Good precision for the sensor application was also obtained with a reproducibility of 7.58% for Pd(II), 6.31% for Pt(II) and 5.37% for Rh(III), for three measurements.

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CYSTEAMINE MODIFIED POLY (8-ANILINO-1-NAPHTHALENE SULPHONIC ACID)/ZINC OXIDE NANOBIOSENSORS FOR STUDYING THE ANALYTICAL BIOTRANSFORMATION OF ISONIAZID, A TB TREATMENT DRUG

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Tuberculosis (TB) is a disease that results from infection by *Mycobacterium tuberculosis* which is the most common infecting organism. The Directly Observed Treatment Short Course (DOTS) regime which is a combination of the drugs (isoniazid, ethambutol, pyrazinamide and rifampicin) has contributed significantly towards the decrease in the number of incidences of this disease. However, incomplete implementation of the DOTS campaign has been a major cause of the high occurrences of the drug resistant strains of *Mycobacterium tuberculosis* coupled with the spread of HIV/Aids in tuberculosis-endemic regions. This results from the fact that fully susceptible tuberculosis develops secondary resistance during therapy due to inappropriate dosing of treatment, inadequate treatment, non-adherence to the prescribed regimen or using low quality medication. This study seeks to develop a nanobiosensor to study the biotransformation of the TB drug; Isoniazid based on nanobiosensor systems developed on gold interdigitated electrodes using N-acetyltransferase coupled to cysteamine modified poly (8-anilino-1-naphthalene sulphonic acid)/zinc oxide nanocomposites. The drug testing analyses will be achieved using a 12 multi-channel robotic workstation while CV will be used to collaborate the received data. The surface morphology of nanocomposites will be studied using High-Resolution Transmission Electron Microscopy (HRTEM), High-Resolution Scanning Electron Microscopy (HRSEM) and Atomic Force Microscopy (AFM). On the other hand, elemental analysis of the synthesized nanocomposites will be achieved using proton-Nuclear Magnetic Resonance, Fourier Transform Infra-Red Spectroscopy, Subtractive Normalization Fourier Transform Infrared Spectroscopy (SNFTIR) and Raman Spectroscopy.

Novel LiMnPO_4 Coated With Magnesium-Gold Composite Thin Film - A Possible Material for Lithium Ion Battery Olivine Cathode

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Architecturally enhanced electrode materials for Li ion batteries (LIB) with permeable morphologies have received broad research interests over the past years for their promising properties [1]. However, literature based on modified porous nanorods [2] of LiMnPO_4 is meagre. The goal of this project is to explore lithium manganese phosphate (LiMnPO_4) nanopowder as cathode material and enhance its energy and power density through surface treatment with transition metal (TM) nanoparticles. Nanostructured materials offer advantages of a large surface to volume ratio, efficient electron conducting pathways and facile strain relaxation [3]. The material can store Li ions but have large structure change and volume expansion during charge/discharge processes, which can cause mechanical failure [4]. LiMnPO_4 is a promising, low cost and high energy density (700 W h kg^{-1}) cathode material with high theoretical capacity and high operating voltage 4.1 V vs Ag/AgCl. Li falls within the electrochemical stability window of conventional electrolyte solutions. LiMnPO_4 has safety features due to the presence of a strong P–O covalent bond. The LiMnPO_4 nanopowder was synthesized via a sol-gel method followed by coated with gold nanoparticles to enhance conductivity. The $\text{LiMnPO}_4/\text{Au}$ was then coated onto MgO nanowires for effective improvement of the capacity retention, rate capability and even thermal stability of the LIB cathode material. MgO is a typical wide band gap insulator, thus, the electronic and optical properties of MgO nanowire was sufficient for the increase in the lithium ion diffusion. The nanostructured composite consisting of the pure cathode material and a conductive additive on the surface, allowed the utilization of theoretical capacity [5]. The pristine LiMnPO_4 and $\text{LiMnPO}_4/\text{Mg-Au}$ composite were examined using a combination of spectroscopic and microscopic techniques along with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Microscopic results revealed that the $\text{LiMnPO}_4/\text{Mg-Au}$ composite contains well crystallized particles and regular morphological structures with narrow size distributions. The composite cathode exhibits better reversibility and kinetics than the pristine LiMnPO_4 due to the presence of the conductive additives in the $\text{LiMnPO}_4/\text{Mg-Au}$ composite. The composite cathode material ($\text{LiMnPO}_4/\text{Mg-Au}$) with improved electronic conductivity holds great promise for enhancing electrochemical performances, discharge capacity, cycle performance and the suppression of the reductive decomposition of the electrolyte solution on the LiMnPO_4 surface. This study proposes an easy to scale-up and cost-effective technique for producing novel high-performance nanostructured LiMnPO_4 nanopowder cathode material.

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A novel titanium dioxide modified polyaniline/polymethyl methacrylate-based MnP nanobiosensor for detection of bisphenol A

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Bisphenol A (BPA) is one of the most internationally investigated endocrine disrupting compounds, following the adverse effects it poses on human health and the environment. Although regulatory bodies have set a minimum tolerable daily intake value (TDI) of 0.05 mg/kg body weight, many studies have reported different negative effects of bisphenol A exposure at concentrations much lower than the set value. Therefore, development of fast, reliable quantitative detection methods for this compound is very crucial. This study developed a biosensor based on a novel nanocomposite of polyaniline doped with polymethyl methacrylate and titanium dioxide nanoparticles. The voltammetric results showed that the nanocomposite had enhanced electroactivity which is favourable for faster electron transfer between the enzyme electrode and the sample under detection. Also, the optical band gap of 2.02 eV reveals that the nanocomposite is biocompatible for non-destructive biomolecule hosting. The nanobiosensor was fabricated by immobilization of MnP, a fungal enzyme well-known for degradation and catalytic oxidation of phenolic compounds in a wide pH range. The sensitivity of the MnP biosensor system towards different concentrations of bisphenol A was investigated using cyclic voltammetry (CV) and square wave voltammetry (SW), where a detection limit of 0.12 nM, within a dynamic linear range from 0.8 to 3.2 nM, was obtained.

Simultaneous anodic stripping voltammetry of trace metals using Bismuth modified glassy carbon electrode

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An anodic stripping voltammetry method for simultaneous measurement cadmium (Cd), lead (Pb), and zinc (Zn) using bismuth modified electrode has been developed. The bismuth modification of the glassy carbon electrode offers an interesting stripping voltammetric performance as compared to the commonly used mercury-film electrodes. This electrode was evaluated using stripping voltammetric measurements PPB levels of the metals in 0.1 M acetate buffer (pH 4.5) a supporting electrolytes that presented a low background. The voltammograms had well resolved peaks at -1.2, -0.8, and -0.56 V for Zn, Cd, and Pb, respectively. A linear range over a 1000 fold was observed in all the metals. The bismuth-coated electrode offered a wider potential window (-1.2 V to -0.4 V), thus enabling possible simultaneous quantification of all metals. The limits of detections were found to be 3.75 µg/L for Cd, 15.52 µg/L for Pb, and 16.26 µg/L for Zn. In the presence of copper, all the metal currents were decreasing, and after addition of 75 µg/L of copper in the cell containing 50 µg/L of each metal, the current responses of Cd, Pb, and Zn were decreased by 67 %, 12 %, and 88 %, respectively.

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Investigating the influence of heat treatment on the performance of Pt-M (M= Ru, Sn) catalysts supported on multi-walled carbon nanotubes and metal oxides for direct methanol fuel cell (DMFC) applications

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This study investigated the influence of heat treatment on PtRu and PtSn electrocatalysts, synthesized using the polyol reduction technique for DMFC applications. These electrocatalysts were supported on MWCNTs, TiO₂ and MoO₂. Carbon black such as Vulcan XC-72 was used for baseline study. X-ray diffraction (XRD) revealed that all catalysts have predominantly the face-centred cubic lattice structure of Pt and high resolution transmission electron microscopy (HRTEM) showed spherical nanoparticles distributed on the support material and an increase in particle size was observed after heat treatment (HT). Cyclic voltammetry (CV) measurements revealed PtSn/MWCNT-HT exhibit a high ECSA (34.77 m²g⁻¹) than all the prepared supported catalysts followed by PtRu/MWCNT-HT (26.66 m²g⁻¹), PtRu/TiO₂-HT (1.87 m²g⁻¹), PtSn/TiO₂ (1.47 m²g⁻¹), PtRuMoO₂-HT (6.1 m²g⁻¹) and PtSn/MoO₂-HT (6.4 m²g⁻¹). Heat treatment proved in this study to be a necessary step in enhancing the activity of the prepared catalyst. PtSn was also observed to be a better performing catalyst than PtRu for the cathode of a DMFC regardless of the support material it was dispersed on.

Electrochemical Behaviour of Cr and W Fischer carbenes: a comparative study

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The first transition metal complex containing a metal–carbon double bond, $(\text{CO})_5\text{W}=\text{C}(\text{Ph})(\text{OMe})$, was synthesized by Fischer and Maasböl in 1964.¹⁰ The reactivity of these Fischer-type complexes can be fine-tuned by modification of either the carbene substituents, the ligands attached to the metal or the metal itself. The Fischer-type complexes were proven to be valuable species in organic syntheses and in catalytic processes.¹¹ An electrochemical study of a series of Fischer carbene complexes of chromium showed that the Cr-carbene complexes generally exhibit two one-electron oxidation processes, namely Cr(0) to Cr(I) to Cr(II).¹² Fischer carbene complexes of wolfram, however, are oxidized in two irreversible two-electron oxidation processes, namely W(0) to W(II) to W(IV).¹³ The first reduction process observed for both the W and Cr carbenes is a one-electron process located on the carbene ligand. The electrochemical behaviour of a series of substituted Cr and W Fischer carbenes will be compared in this study. Results will be complemented by density functional theory calculations, in order to predict and understand the oxidation and reduction potentials.

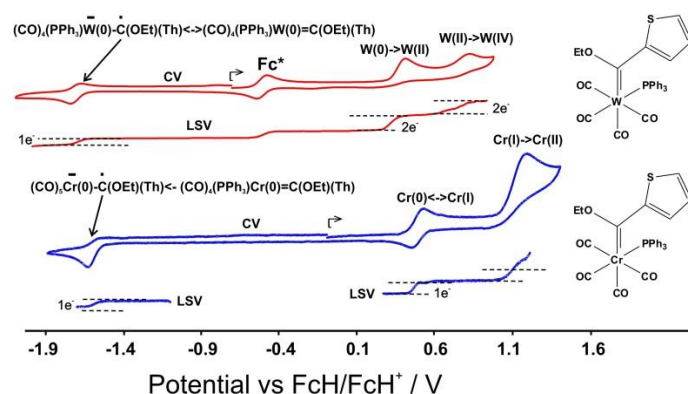


Figure 1: Comparative cyclic voltammograms (CV) and linear sweep voltammogram (LSV) of *c.a.* 0.0005 mol dm⁻³ solutions of the indicated carbenes in CH₃CN / 0.1 mol dm⁻³ [n(Bu₄)N][PF₆] on a glassy carbon-working electrode at a scan rate of 0.100 V s⁻¹. CV peaks due to the internal standard used, are marked Fc*. Scans initiated in the positive direction as indicated with arrows.

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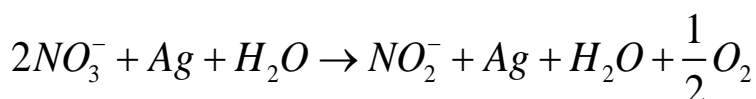
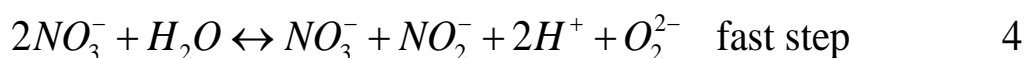
Degradation of nitrates with Silver nanoparticles

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Nitrate's pollution is a major problem worldwide, because of their wider application, high solubility, and health hazard especially to babies (baby syndrome). Recently use of nanomaterials in remediation has been extensively studied. This is a result of their physical and chemical properties (catalytic) resulting in increased rates. This study looks at the degradation pattern of nitrites (NO_2^-) and nitrates (NO_3^-) by silver nanoparticles (AgNPs). The following parameters were investigated time, pH, age and temperature. Monitoring of the amounts of nitrite and nitrite was done by UV visible spectroscopy absorbance at 350 nm, and 290nm respectively. These detection methods were evaluated and applicable analytical parameter determined for each analyte. In the presence of AgNPS a change in the absorbance of the Nitates and nitrates were observed over time as well as in different pH solutions. However, they were no observable difference between freshly prepared AgNPS and the 1 month metals. The nitrites and nitrates degradation in the presence of AgNPs was observed after 10 minutes and they was minimum effect from temperature and pH strongly indicating that the reactions are involved are as follows:



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**Extraction and characterization of hemicellulose from wild species of Cactus plant
(*Opuntia ficus indica*)**

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A novel hemicellulose possessing rare sugars namely lyxose, D-(-)-lyxofuranose, α-D-(-)-lyxopyranose was isolated from cactus (*Opuntia ficus indica*) pads. The extraction procedure employed 2M NaOH in 70% ethanol as an extraction media, followed by filtration, acidification, and then precipitation, washing with the different concentrations of ethanol and freeze drying. The isolated hemicellulose was insoluble in water and other organic solvents. Identification of sugars was done with the help of gas chromatography coupled with time of flight mass spectrometer (GC x GC-ToFMS). Besides lyxose and its isomers, the GC-MS spectra revealed the presence of other sugars including, xylose, mannose, arabinofuranose, arabinopyranose and mannonic acid.

Key words: Hemicellulose, cactus, *Opuntia ficus indica*, lyxose, rare sugars, GC x GC-ToFMS

Determination of redox potential of rooibos tea extract via cyclic voltammetry analysis

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Rooibos tea is produced from the leaves and fine stems of *asphaltus linearis*, a fynbos endemic to South Africa, by fermentation and sold to more than 37 countries worldwide. Many studies have been done to investigate potential health benefits of rooibos tea arising from its antioxidant phenolic compounds. The rooibos tea extract found commercial applications in beverages as preservative and in personal care products as antiaging material due to its antioxidant properties. In recent years, some publications have reported that tea extracts can be used as replacement to the poisonous chemical reductants in the synthesis of silver, copper and iron nanoparticles. But, there has not yet been any work showing utilization of the rooibos tea extract in this field. The current study aimed at measuring the redox potential of rooibos tea to see if it is suitable to be a reductant in the green synthesis of iron nanoparticles. Cyclic voltammetry, an electrochemical analysis technique which is cheap and simple, was used for this purpose. An established cyclic voltammetry method dealing with tea extracts was followed during the measurements. The cyclic voltammogram of rooibos tea extract showed a sharp peak at +0.25 V. According to the literature, this potential is enough to reduce Fe(III) to Fe(II) but not Fe(II) to Fe(0) as autooxidation process rapidly converts Fe(II) to Fe(III).

Electrochemical Study of Epinephrine at Metal Oxide doped Phthalocyanine supported on Carbon Nanotubes Sensor Platform.

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Epinephrine (EP) belongs to the family of inhibitory neurotransmitters in mammalian central nervous systems where it acts as a cellular chemical messenger and many diseases are related to the change of its concentration. Determination of the level of EP is important for diagnosis of Parkinson's disease, among other mental disorders. EP drugs are also used to treat anaphylactic shock, bronchial asthma and organic heart disease. Therefore, a quantitative determination of EP in body fluids has become increasingly significant. Electrochemical sensing has been proven as simple analytical method that can determine the presence of a wide range of substances at relevant concentration levels with sufficient selectivity, sensitivity, reproducibility, and they are small, inexpensive, relatively simple to fabricate, easily implantable, and can provide real-time measurements.

In this study, the electron transfer and catalytic properties of glassy carbon electrode (GCE) modified with Phthalocyanine (Pc) doped with zinc oxide (ZnO) and iron (II,III) oxide (Fe₃O₄) nanoparticles respectively, supported on multi-walled carbon nanotubes (MWCNT) was investigated. Successful synthesis of the nanomaterials was confirmed using spectroscopic and microscopic techniques such as FTIR, UV-vis, Raman, XRD, EDX, SEM and TEM, while successful modification/fabrication of the sensors was confirmed using cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). The developed sensors include GCE-MWCNT, GCE-Pc, GCE-Fe₃O₄, GCE-ZnO, GCE-MWCNT-Pc-ZnO, and GCE-MWCNT-Pc-Fe₃O₄. Electron transfer properties of the modified GCE was investigated in 0.1 M PBS (pH 7.0) and 5 mM Ferri/Ferro ([Fe(CN)₆]^{3-/4-}) redox probe using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The modified electrode was applied for the determination of EP in 0.1 M PBS (pH 7.0) using CV, differential pulse voltammetry (DPV) and EIS with excellent electrocatalytic activity towards the electrochemical oxidation of EP exhibiting a large peak current and shift of peak potential compared to unmodified electrode.

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INTERROGATING THE USE OF A PORTABLE POTENTIOSTAT FOR ASCORBIC ACID DETECTION ON PHTHALOCYANINE MODIFIED ELECTRODE

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Electrochemical methods have the advantage of on-site application, low cost and simplicity. Recent advancement in electronics have resulted in the miniaturization of electrochemical workstation which further enhances their application. This work interrogates the applicability of a novel, miniaturised and low cost potentiostat in the market called cheapstat¹, by applying it to the determination of ascorbic acid. Ascorbic acid is a very important biochemical molecule and its deficiency in the human body causes scurvy. It is also used as antioxidant and preservatives. A gold screen printed electrode is modified with iron phthalocyanine via self assembly²⁻⁴. The modified electrode was characterized electrochemically in $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ and $[\text{Fe}(\text{CN})_6]^{3-/4}$ redox probes and used in the voltammetric detection of selected analytes such as ascorbic acid. The modified electrode gave enhanced currents in the redox probe in comparison to the pristine gold electrode and electrocatalytic oxidation of ascorbic acid was also observed on the modified electrode owing to the presence of the iron phthalocyanine. The Cheapstat compared very fairly with the well-known potentiostat based on the statistical analysis of the results thus indicating its suitability for sensor application. Cheapstat is cheap, runs on a free java software and is usb/battery controlled. It is therefore suggested that Cheapstat can therefore be used for low end, on-site and undergraduate electrochemical studies.

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EXFOLIATED GRAPHITE/TUNGSTEN TRIOXIDE NANOCOMPOSITE, AS AN ADVANCE ELECTRODES FOR THE PHOTOELECTROCHEMICAL DEGRADATION OF EOSIN YELLOW FOR SYNTHETIC WASTEWATER

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Advance oxidation processes (AOP), of which photoelectrochemical oxidation is a subset, are a green approach to water treatment. As a result, several materials have been prepared and used as electrodes for the photoelectrochemical degradation of pollutants in water. In this work, WO₃ nanoparticles and exfoliated graphite (EG) were prepared by sol-gel and modified hummer's methods respectively. The EG-WO₃ was prepared by incorporating the WO₃ into EG by wet solution method. The materials were characterized using scanning electron microscopy (SEM), thermogravimetry and differential thermal analysis (TGA), Brunauer-Emmett-Teller surface area analysis (BET), infrared (IR) spectroscopy and X-ray diffraction (XRD). The applicability of the EG-WO₃ as photoanode was investigated by the photoelectrochemical degradation of eosin yellow as a model for organic pollutants in 0.1 M Na₂SO₄ (pH 7) solution at a current density of 5 mA cm⁻². The FTIR, XRD and Raman data revealed the formation of the nanocomposite. The XRD patterns further points out that the WO₃ nanoparticle contains both monoclinic and tetragonal phases. Photoelectrochemical studies with the EG-WO₃ electrode showed significant decrease in the dye concentration (20 ppm) compared the bare EG or WO₃. This shows that the WO₃ nanoparticle in the EG-WO₃ composite enhanced the degradation efficiency of the eosin yellow. Thus, the EG-WO₃ electrode is applicable for the photoelectrochemical oxidation of organic pollutants, especially organic dyes in water.

Keywords: exfoliated graphite, WO₃ nanoparticle, advance oxidation processes, dyes, eosin yellow

PREPARATION, CHARACTERIZATION AND APPLICATION OF EXFOLIATED GRAPHITE BASED ELECTRODES IN THE ELECTROCHEMICAL DETECTION OF ARSENIC (III)

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Arsenic is a very toxic metal that has gained a lot of attention worldwide due to its adverse health effects such as keratosis, skin lesions and cardiovascular diseases [1]. It is therefore very important to monitor the level of arsenic for compliance with the WHO limit of 10 ppb. This research is aimed at developing a simple, low cost, rapid, and highly sensitive method based on exfoliated graphite (EG) for detection of arsenic in water. Exfoliated graphite was prepared by intercalating natural graphite with strong acids, washed and finally exposed to a thermal shock of 800 °C [2]. The EG was characterized with SEM, EDS, XRD, FTIR and Raman spectroscopy. SEM and EDS proved the formation of EG material with accordion-like structure and presence of oxygen and sulphur from the intercalates. XRD showed low diffraction peak intensity of EG due to decreased crystallinity and increase crystal defects, proving formation of EG material. The EG was pressed into pellets without any binder and used for fabrication of electrodes. The electrodes were modified with AuNPs cycling the potential from -0.2 V to 1.2 V for 15 cycles and electrochemically characterized them in $[\text{Fe}(\text{CN})]^{3-/4-}$ probe using CV within a potential range of -0.25 V to 0.7 V. The modified EG electrodes showed an enhanced peak over bare EG electrodes and this is an indication of large surface area to volume ratio shown by AuNPs [3]. Square wave anodic stripping voltammetric technique was used to detect As(III) in water (in 0.1M KNO_3 as supporting electrolyte) after optimization of the following parameters: deposition potential, deposition time, pH, frequency and Amplitude. EG-AuNPs electrodes detected As(III) to a limit of ppb level. The EG-AuNPs showed excellent sensitivity and thus has the potential for the detection of other heavy metals and real water sample analysis.

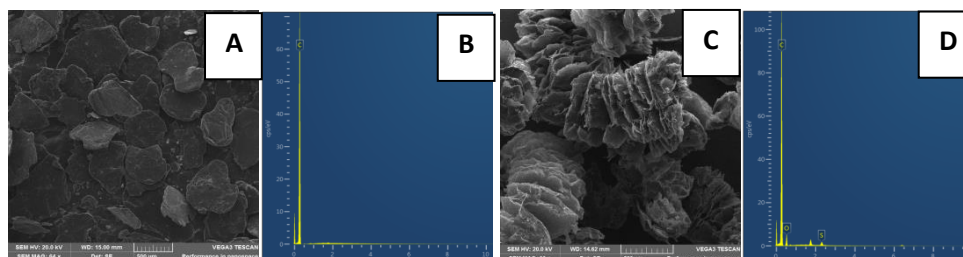


Figure 1: SEM images and EDS spectra of natural graphite flakes and exfoliated graphite.

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ELECTROCHEMICAL DETECTION OF CHLOROPHENOLS ON NICKEL PHTHALOCYANINE MODIFIED EXPANDED GRAPHITE ELECTRODE

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Chlorophenols are well known priority organic pollutants that are persistent in water. It is therefore important to develop simple methods of detecting and monitoring these pollutants in water. Electrochemical methods offer a simple route to the detection of organic and inorganic pollutants in water. However, when the analyte is a phenol, this plausible technique is hampered by fouling. It is believed that modified electrodes with electrocatalytic properties may mitigate this fouling challenge and improve the sensitivity of phenol sensing. In this light, we present the sensing of Chlorophenol on a novel Nickel Phthalocyanine (NiPc) modified expanded graphite electrode (EG). Natural graphite was intercalated with acids, and then subjected to a high temperature shock to yield expanded graphite. This low density multi layers of graphene sheet was compressed (at high pressure) and fabricated into an expanded graphite electrode (EG). We took advantage of the fact that metallophthalocyanines (MPc) adsorb strongly on graphite and carbon-based electrode materials at monolayer levels, leading to obtaining “molecular phthalocyanine electrodes” which exhibit electrocatalytic activity toward several electrochemical reactions¹. The EG electrode was modified with a synthesised NiPc² by electrodeposition and drop coating to form the EG/NiPc electrode. The NiPc film and EG/NiPc electrode were characterised using electron microscopy and electrochemistry. The presence of the NiPc film showed marked current enhancement over the EG in selected redox probe. The electrode also showed electrocatalysis in the presence of ascorbic acid. The EG/NiPc electrode was used to detect 3-CP and 4-CP in water. The effect of fouling was markedly reduced on the modified electrode. A low detection limit in the sub micromolar level was obtained for both chlorophenols. Furthermore, the electrode was able to give separate signal for 3 and 4 CP in a solution of their mixture. This EG/NiPc is easy to prepare and this electrode offers new possibilities in phenol sensing.

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SYNTHESIS AND APPLICATION OF DENDRIMER FUNCTIONALIZED CARBON NANOTUBES AS PLATFORMS IN ELECTROCHEMICAL SENSING.

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The quest for novel nanomaterial with electrochemical application is an on-going research. This work presents the synthesis, characterisation and application of poly (propylene imine) dendrimer functionalised multi-walled carbon nanotube (CNT) in electroanalysis. The multiwalled CNT was carboxylated with strong acids. Poly (propylene) imine dendrimer (PPI) was then coupled to the functionalised CNT with the aid of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) / N-hydroxysuccinimide (NHS) to form CNT-PPI. The materials were characterized with FTIR, Raman spectroscopy, SEM, XRD and electrochemistry. FTIR revealed the characteristic peaks for carbonyl indicating the formation of amide bond linking the dendrimer to the CNT. FTIR peak of primary amine for primary amine was also observed and this shows that the nanocomposite has primary amine sites available for electrodeposition on glassy carbon electrode. The dispersion of the CNT in aqueous solvent was enhanced owing to the presence of the dendrimer. The nanocomposite (CNT-PPI) was then used to modify glassy carbon electrode via electrodeposition and drop coating. The electrochemical applicability of the glassy carbon modified CNT-PPI electrode was explored by developing a sensor for analytes such as chromium (VI) ion and dopamine. Chromium is an economically important metal with high biological toxicity when it occurs in the hexavalent state. Cr (VI) was detected using square wave anodic stripping voltammetry. The sensor was very sensitive towards Cr (VI) with and without interferences.

PHOTOELECTROCHEMICAL APPLICATION OF SILVER OXIDE - ZINC OXIDE NANOCOMPOSITE DOPED REDUCED GRAPHENE OXIDE ELECTRODE FOR WATER TREATMENT

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In the search for novel and efficient electrochemical materials as electrodes for photoelectrochemical degradation and mineralization of organic pollutants in water treatment, Ag₂O-ZnO-RGO electrode was synthesized, characterized and photoelectrochemically applied in the degradation and possible mineralization of organic pollutants in water treatment process. The ZnO and Ag₂O-ZnO nanoparticles were synthesized by a facile one-step co-precipitation method followed by calcinations at 400 °C. The reduced graphene oxide (RGO) which is highly stable, thermally and electrically conductive was synthesized via Hummers method and then reduced using ascorbic acid. ZnO was used because of its low cost, non-toxicity, light absorption, photochemical and catalytic properties¹. The p-n heterojunction of Ag₂O and ZnO helped to enhance charge separation and transfer¹. Also, the absorption of light in the visible spectrum by ZnO was improved by surface plasmon resonance effect due to the formation of Ag-Ag₂O in photocatalytic degradation of organic pollutants^{2,3}. The characterizations were done by cyclic voltammetry, electrochemical impedance spectroscopy, FTIR, Raman spectroscopy, scanning electronic microscopy (SEM), energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD) and thermal gravimetric analysis (TGA). The photoelectrochemical applicability of the Ag₂O-ZnO-RGO as photoanode material was tested by the photoelectrochemical degradation of orange II dye as target organic pollutant in 0.1 M Na₂SO₄ solution at a current density of 10 mAcm⁻².

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SCALE REDUCTION IN COOLING WATER PIPES: EXPERIMENTAL AND MODELLING APPROACHES

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A comprehensive understanding of the influence of natural organic matter (NOM) on metal-complex formation and their stabilities, speciation, and inhibition of scaling (by scale-forming species) is currently lacking. This study reports characteristics and role of NOM with respect to metal complexation. The latter is known to minimize scaling potential through the removal of metal ions in solution. The metal-NOM complexation studies were carried out using experimental and modelling approaches. The experimental investigations involved the application of voltammetric, spectroscopic and chromatographic techniques. The characteristic NOM fractions (humic substances) in water samples were analysed in the laboratory using gas/liquid chromatography-mass spectrometry and fluorescence excitation emission spectroscopy (FEEM). After NOM fraction quantification, accurate speciation and simulative model measurements were generated through using PHREEQC code. Model results showed that new stable complex species such as CaFulvate, BaFulvate, MgFulvate, ZnFulvate, CuFulvate and FeFulvate⁺ were formed. The PHREEQC based simulations were achieved using the modified Tipping and Hurley with Windermere's Humic Acid Model (T_H-WHAM). Modelling the formation of these discrete chemical complexes, showed a reduction in the concentration of free calcium ion in solution, hence a decrease in the scaling potential. Saturation index output results indicated the mineral phases likely to precipitate with scale formation during cooling water process.

Keywords: Cooling water, Modelling, PHREEQC, Complexation, Natural Organic Matter

Synthesis, Spectroscopic And Electrochemical Characterization Of Ternary AU/PANI/TiO₂ Nanocomposite.

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A ternary chemically modified electrode is constructed based on polyaniline doped with titanium (IV) oxide nanoparticle-modified gold electrode (Au/PANI/TiO₂). The structure, morphology of the nanomaterials was characterized by UV/Vis spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, and transmission electron microscope. Cyclic voltammetry techniques and electrochemical impedance (EIS) were used for the electrochemical characterization of the modified sensors. The cyclic voltammograms obtained at the electrodes Au, Au/TiO₂ and Au/PANI/TiO₂ respectively showed a pair of electrodes peaks attributed to the Fe(CN)₆⁴⁻/[Fe(CN)₆]³⁻ redox process. Au/PANI/TiO₂ electrodes gave a higher current response of anodic peak currents (I_{pa}) 28.7 μA when compared to 26.9 and 22 μA for Au and Au/TiO₂ electrodes respectively. The electrochemical impedance study for the electrodes reveal that the electron transport is faster with Au/PANI/TiO₂ modified electrode because of charge transfer resistance R_{ct} value 2.98 kΩ which is lower than 7.01 and 45.3 kΩ for the Au and Au/TiO₂ respectively. The stability of the nanocomposites was also carried out. Further studies on electrocatalysis of the nanocomposite will as well be studied.

Keyword: Ternary, Au-electrode, PANI, TiO₂, Cyclic voltammetry and Electrochemical impedance

INTERROGATION OF Ag NPs - DOPED POLYANILINE'S POTENTIAL FOR USE AS AN ELECTROCHEMICAL TRANSDUCER

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The chemical modification of electrodes has triggered an interesting consideration in analytical chemistry in relation to electrochemical detection of organic compounds and sensor development. In this study platinum (Pt) electrode surface was modified by polyaniline (PANI) via electropolymerization in the absence and presence of silver nanoparticles (Ag NPs). This resulted in formation of Pt/PANI and Pt/PANI/Ag NPs electrodes. The impact parameters such as surface coverage, film thickness and band gap, which are very scarce in the literature, were determined. These parameters can directly or indirectly affect the electron transfer kinetics between the adsorbed species and the structure of the underlying electrode, the stability of the sensor and the nature of the diffusion or kinetics limiting the current produced. The surface coverage values were determined from cyclic polymerization as 3.00×10^{-09} and 10.00×10^{-09} mol/cm² and for polymer film thickness are 5.60×10^{-08} and 18.80×10^{-08} cm for Pt/PANI and Pt/PANI/AgNPs respectively. Electrochemical evaluation of the modified electrode was done by cyclic voltammetry (CV) in monomer-free electrolyte solution. Spectrophotometric (Fourier transform-infrared (FTIR)) technique was used to determine the resultant structural behaviour of the modified electrode surface. High conductivity was achieved with Pt/PANI/Ag NPs compared with bare Pt and Pt/PANI. The conductivity trend is as follows: Pt < Pt/PANI < Pt/PANI/Ag NPs. Spectrophotometric results indicated that the chemical structure of the polyaniline is retained in the electrode modifications. However, minor peak shifts observed are indicative of physio-chemical interactions between PANI and Ag NPs. These features of PANI/Ag NPs can guarantee possible applications of the modified Pt electrode.

Electrochemical studies of conjugated dienes [1.3-Cyclohexadiene (CHD), 1.3-Cyclooctadiene (COD), 2-Methyl-1.3-Butadiene (MBD) and trans-1.3-Pentadiene (PD)] in acetonitrile for development of organic sensor.

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The detection of dienes in fuels is important as they readily polymerise and form gum in fuel tanks. The electroactivity of the four conjugated dienes (1.3-Cyclohexadiene CHD, 1.3-Cyclohexadiene COD, Trans-1.3-pentadiene PD and 2-Methyl-1.3-butadiene MBD) was studied by cyclic voltammetry with unmodified Pt electrode in tetrabutylammonium perchlorate (TBAP)/acetonitrile solution. Severe electrode fouling was observed when steady state amperometric detection of CHD as a representative diene, was performed on Pt electrode. Randel-Sevčik analysis of the cyclic voltammetry of the conjugated dienes on Pt electrode gave diffusion coefficient (D_{ox}) values of 10.65 cm²/s, 9.55 cm²/s, 3.20 cm²/s and 3.96 cm²/s for CHD, COD, PD, and MBD, respectively. The corresponding detection limits ($3\sigma_{n-1}$) were 0.0106 M, 0.0111 M, 0.0109 M, and 0.0107 M.

Luciferase Biosensor for the determination of polycyclic aromatic hydrocarbons (naphthalene and fluoranthene)

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Abstract:

For the construction of a biosensor the spectroscopic and electrochemical properties of the enzyme, Photobacterium Vibrio fisheri luciferase and the analytes i.e naphthalene and fluoranthene were evaluated. Fluorescence spectroscopy studies were carried out to characterize the enzyme's bioluminescence response in phosphate buffer (PBS) at pH 7. Luciferase showed an absorption peak at 340 nm. The bioluminescence properties of the enzyme with the analytes were explored by fluorescence spectroscopy. The absorption peak at 340 nm gradually decreased as the concentration of each analyte was increased respectively. Electrochemical characterization and immobilisation of the enzyme; Photobacterium Vibrio fisheri luciferase, and its application as a biosensor for selected polycyclic aromatic hydrocarbons was investigated. The enzyme was electroactive in PBS (pH 7) with two reversible redox couples at $E^{\circ'} = +110$ mV and $E^{\circ'} = +730$ mV and was observed to have a diffusion coefficient of 1.1×10^{-12} cm²/s. The surface coverage was calculated to be 1.50×10^{-13} moles/cm² based on Brown-Anson model. The mass changes due to the addition of each analyte were measured by Electrochemical Quartz microbalance (EQCM). % Inhibition was calculated as an indicator of analyte interaction with the immobilised enzyme, in order to evaluate the sensitivity of the enzyme binding. Electrochemical impedance spectroscopy studies were done at a fixed potential of -730 mV over the frequency range 100 mHz to 1 kHz. The R_{ct} values increased for each analyte, naphthalene and fluoranthene as the concentrations of each analyte was increased. The system thus became less conductive as the amount of PAHs was introduced to the PAA/PPy/LUC biosensor. R_{ct} was identified as the parameter to most appropriately model the binding event between luciferase and the two analytes.



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