Book of Abstracts

EMS 1

Electrochemistry Masterclass Series 1

11th April 2024

Venue: School of Public Health, University of the Western Cape

Sponsored by:

Programme

Time	Talks	
9:00 – 9:30	**Tea and Registration**	
9:30 – 10:00	Welcome	Prof Omotayo Arotiba
10:00 – 11:00	Presenter	**Dr Tumaini S Mkwizu** *Advanced Instrumentation and Techniques for Electrochemical Research*
11:00 - 11:30	**Tea break**	
11:30 – 13:00	**Flash Poster presentations**	
Duduzile Nkosi	An electrochemical immunosensor on a carbon nanofiber/gold nanoparticles platform for the detection of alpha-feto protein cancer biomarker.	
Irvin Noel Booysen	An electrospun nanofiber composite utilized as an electrocatalyst for the detection of acetaminophen in multifarious water samples	
Masego Ramonyai	Investigating the role of dipicolinic acid on the the simultaneous analysis of Copper and Bismuth.	
Nolwazi Gazu	Polyaniline-Gadolinium Telluriselenide-based Aptasensor for SARS-CoV-2 spike glycoprotein	
Nyasha Midzi	An electrochemical sensor for caffeine based on graphene quantum dots-manganese oxide nanocomposite modified electrode	
Sesethu Makaluza	Quantitation of Nicotine in Flavored Hookah Pipe Tobacco at a Nitrogen-Doped Carbon Nanosheet/Poly(amidoamine) Dendrimer-based Electrochemical Sensor	
Kehinde D. Jayeola	In-situ fabrication of a Z-scheme $Bi_2O_2S/NiTiO_3$ heterojunction photoanode for the photoelectrochemical degradation of sulfamethoxazole in wastewater	
13:00 – 14:10	Presenter	**Prof Carlos Sanchez-Sanchez** *Scanning electrochemical microscopy*
14:10 – 15:00	**Lunch Break**	

15:00 – 15:45	Presenter	**Prof Frank Marken** *Fundamentals in Electrode Kinetics – Part 1*
15:45 – 16:00	**Tea Break**	
16:00 – 16:15	Presenter	**Prof Frank Marken** *Fundamentals in Electrode Kinetics – Part 2*
16:45 – 17:00	Closing Speech	Omotayo Arotiba
17:00	Transport provided to The Wijnlanden Uitzicht Stellenbosch and back. All In – person delegates.	

Advanced Instrumentation and Techniques for Electrochemical Research

Dr Tumaini S. Mkwizu

Bruno Steiner Lab Consultancy

ABSTRACT

Modern electrochemical research is rapidly evolving as a result of advances in instrumentation and multipurpose software capabilities offered by research-driven laboratory equipment vendors. This talk will highlight state-of-art capabilities of BioLogic electrochemical instruments with special focus on single-channel and mutli-channel potentiostat-galvanostats as well as battery cyclers typically deployed for execution of direct current and/or alternating current electrochemical techniques on single- or multi-electrode cells. Flexible modes of measurements and synchronisation with a wide range of external devices will also be demonstrated. A wide range of examples will be presented for voltamperometric techniques (such as linear sweep voltammetry, cyclic voltammetry and pulsed voltammetry), chronoamperometry, chronopotentiometry, and electrochemical impedance spectroscopy. Moreover, examples of automated experimental configurations for variable temperature control and data acquisition as well as synchronisation of rotating disk electrode measurements will be described. A survey of typical data analysis tools will be highlighted, focusing on extraction of electrochemical parameters of interest in electroanalytical cells and electrochemical energy storage and conversion cells.

Scanning Electrochemical Microscopy (SECM) for Studying Electrocatalytic Reactions

Dr. Carlos M. Sánchez-Sánchez

Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE), 4 place Jussieu, F-75005, Paris, France

Biodesign AL1-10-14

Electrocatalytic reactions are those in which either reactants, intermediates or reaction products are specifically adsorbed on the electrode surface to lower the energy barrier of the reaction. However, there are not many electrochemical techniques that allow to study this type of reactions and their mechanisms. For this reason, the scanning electrochemical microscope (SECM) represents a powerful electroanalytical tool for catalyst imaging either for energy or environmentally relevant reactions. SECM in comparison with other scanning probe microscopies provides the great advantage of being able to map the chemical reactivity of the substrate material (some examples are shown below). Moreover, SECM has been revealed as a useful technique for the reaction mechanism elucidation, thanks to its ability for the detection of reaction intermediates. Thus, SECM has been successfully used as a screening technique for correlating either catalyst chemical composition vs. reactivity or catalyst surface structure vs. reactivity for different reactions. However, nowadays, the variety of electrocatalytic reactions studied by SECM is limited. For this reason, a great effort is focused on developing new modes of SECM in order to increase its present scope as a useful tool in catalysis. In particular, we have recently introduced a new micropipette-based mode for locally releasing the electroactive species under steady-state conditions and forced convection transport, which overcomes most of the limitations present in other SECM modes. In this lecture, I will review the main features of SECM and discuss some of the most relevant results characterizing different electrocatalytic materials.

Fundamentals in Electrode Kinetics

Frank Marken

University of Bath
Bath BA2 7AY, England
F.Marken@bath.ac.uk

This lecture will provide a first introduction and overview of basic electrode processes. The concept of polarization of an interface is considered and the reasons for electron transfer are dissected. Fundamental experimental design aspects are explained.

Content in Keywords:
- Polarization effects at interfaces
- Types and structure of interfaces
- Effect of liquid media
- The double layer and electron transfer
- The design of the electrochemical cell
- Transport generally (types, and Fick's laws)
- The concept of the rate limiting process in terms of dimensional analysis

Further Reading:
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An electrochemical immunosensor on a carbon nanofiber/gold nanoparticles platform for the detection of alpha-feto protein cancer biomarker.

D. Nkosi[a,b], F.O.G. Olorundare[a], and O.A. Arotiba[a,b]

[a] Department of Applied Chemistry, University of Johannesburg, Doornfontein 2028, South Africa

[b] Centre for Nanomaterials Science Research, University of Johannesburg, South Africa

dnkosi@uj.ac.za.

Functionalised carbon nanofiber and gold nanoparticles were immobilised through drop drying and electrodeposition techniques respectively on a glassy carbon electrode (GCE). AFP antibody was immobilised on the platform overnight followed by blocking of nonspecific binding sites with bovine serum albumin (BSA) for 4 h. The AFP antigen was incubated on the platform for 40 min at 35 $^{\circ}$C for the antigen – antibody interaction[1-3]. CNF and AuNPs were characterised by electron microscopy and Fourier transform infrared (FTIR) spectroscopy. The modified electrodes and the immunosensor were characterised by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The electrochemical response of the GCE/CNF/AuNPs electrode and the resulting immunosensor was significantly enhanced by the nanocomposite of CNF and AuNPs. The electrochemical immunosensing measurement for AFP was carried out under optimal conditions at a concentration range from 0.005 to 500 ng mL^{-1} in 5 mM ferri/ ferrocyanide solution. A low limit of detection of 0.50 pg mL^{-1} from square wave voltammetry (SWV) and 0.48 pg mL^{-1} 1 from EIS measurements were obtained. The immunosensor exhibited good sensitivity, good selectivity, good repeatability, and was stable at 4 $^{\circ}$C over a period of three weeks.

References

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3 C.I. Justino, A.C. Duarte, T.A. Rocha-Santos, Immunosensors in clinical laboratory diagnostics, Adv. Clin. Chem. 73 (2016) 65–108.

An electrospun nanofiber composite utilized as an electrocatalyst for the detection of acetaminophen in multifarious water samples

Booysen IN[a], Mambanda A[a], Shoba S[a]

[a] School of Chemistry and Physics, University of Kwa-Zulu Natal, Pietermaritzburg, South Africa, E-mail: Booyseni@ukzn.ac.za

Keywords: Cobalt phthalocyanine, electrospun nanofibers, carbon nanotubes, acetaminophen, polyaniline.

In the realm of electrochemical sensors, metallophthalocyanines (MPcs) can serve as appropriate synthons to fabricate thin films that act as electrocatalysts on working electrodes for the detection of water pollutants.[1, 2] Herein, the nanofabrication and characterization of new conductive materials, PANI-CoPc-fur (**1**) ((PANI = polyaniline and CoPc-fur = *tetra*-4-(furan-2-methylthiophthalocyaninato)Co(II)) and PANI-CoPc-fur-*f*-MWCNTs (**2**) (*f*-MWCNTs = carboxylic acid functionalized multi-walled carbon nanotubes) are reported.[3] Subsequently, an electrospun nanofiber (ENF) composite of **2**, encapsulated with a polyvinyl acetate shell was fabricated. The resultant core-shell nano conjugated fibres, ENFs-**2** were adsorbed on a glassy carbon electrode (GCE) followed by the immobilization of a permeable adhesion top layer of Nafion (Nf) to render the chemically modified electrode, GCE|ENFs-**2**-Nf. The detection of Acetaminophen (APAP) at the GCE|ENFs-**2**-Nf attained by squarewave voltammetry (SWV) was linear from 10 to 200 µM of APAP and was reproducible (%RSD of 3.2%, $N = 3$), see **Figure 1**. The analytical performance of the GCE|ENFs-**2**-Nf rendered a comparable percentage recovery (104%) with that of liquid chromatography–mass spectrometry (LC–MS) (106%).
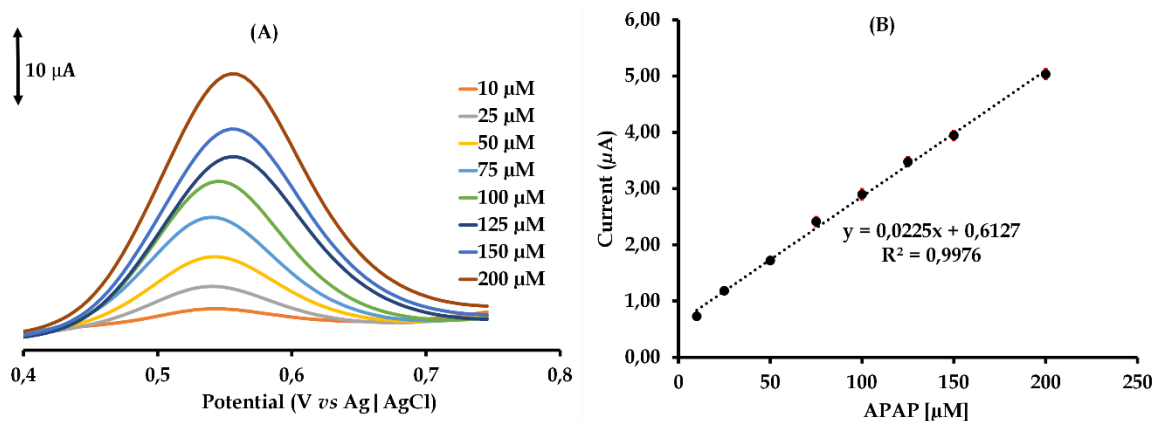

Figure 1: *(A) SWVs were recorded at different concentrations of APAP prepared in 0.1 M PBS (pH 3.11) using the |GCE-ENFs-2-NF. (B) Calibration curve of the current response against APAP concentration (10 to 200 μM).*

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Investigating the role of Dipicolinic acid on the simultaneous analysis of Copper and Bismuth.

Masego Ramonyai, Caren Billing

Email:0719016m@students.wits.ac.za

Keywords: Bismuth, Copper, Interfering ions, Dipicolinic acid.

When studying the effect that possible interfering metal ions such as Cu(II) has on the analysis of Bi(III) in solution, it was clear that the simultaneous analysis of bismuth and copper by anodic stripping voltammetry (ASV) cannot be accurately done since the Bi(III) and the Cu(II) responses greatly overlap.[1] In an effort to separate the overlapping peaks, the introduction of a chelating ligand such as dipicolinic acid (DPA) was investigated. Bi(III) and Cu(II) form stable complexes with dipicolinic acid across a wide pH range, but importantly, the addition of DPA successfully separates the bismuth and copper peaks. This study was done at very low pH (0.3) where the diffusion junction potential is extensive due to the high H^+ concentration and, although hydroxide complexes were avoided for copper, bismuth still readily hydrolyzes at low pH.[2] We have demonstrated in some preliminary studies that the addition of dipicolinic acid (DPA) as a complexing agent delays the hydrolysis of Bi(III). Not only does CuL^+ complex successfully form in the presence of Bi(III), but its peak current (I_p) increased in a linear manner as the concentration was increased. The presence of CuL^+, however, did not significantly affect the analysis of Bi(III) in solution. We have found that the presence of DPA in solution resolves the bismuth peak from the peaks of interfering ions and that ASV is a suitable voltammetric technique for these measurements.

References

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Polyaniline-Gadolinium Telluriselenide-based Aptasensor for SARS-CoV-2 spike glycoprotein

NT Gazu, XG Fuku, BB Mamba, U Feleni*

Institute for Nanotechnology and Water Sustainability (iNanoWS), College of Science, Engineering and Technology, University of South Africa, Private Bag X6, Florida Science Campus, 1709, Johannesburg, South Africa

Corresponding author: felenu@unisa.ac.za

Herein, an electroconductive aptasensor protocol has been developed for the detection of spike glycoprotein. The aptasensor consists of a specific thiolated aptamer (HS-Apt) and a combination of polyaniline (PANI) and 3-mercaptopropionic acid capped gadolinium telluriselenide quantum dots (3-MPA-GdTeSe QDs) incorporated on a glassy carbon electrode. The functional properties of the capping of the quantum dot, PANI was confirmed using Fourier transform infrared spectroscopy. Furthermore, the interaction between the amine functional group of PANI and the carboxylic acid ligand of 3-MPA-GdTeSe was confirmed. Cyclic voltammetry was used to analyse the electrochemical redox properties of the prepared materials prior to application and an enhancement in redox electron transfer was observed at an optimized potential window of $0.3 - 1$ V. Parameters such as pH, scan rate and aptamer incubation were optimized, the latter achieving a 7-minute aptamer incubation time. The PANI|3-MPA-GdTeSe QDs nanocomposite was further used as an interface for HS-Apt for SARS-CoV-2 spike glycoprotein application using square wave voltammetry. A limit of detection and quantification of 0.799 and 2.398 fM was obtained, respectively at a dynamic concentration range of $0 - 0.95$ fM. The response of HS-Apt|PANI|3-MPA-GdTeSe was observed from $0.419 - 0.390$ V with increasing concentration in 0.1 M PBS. COVID-19 may not be considered as the global health emergency; however, the use of this technique could potentially find application in case of future illness outbreaks as an alternative clinical and/or environmental diagnostic tool, as a lower concentration of SARS-CoV-2 spike glycoprotein can be detected using this technique.
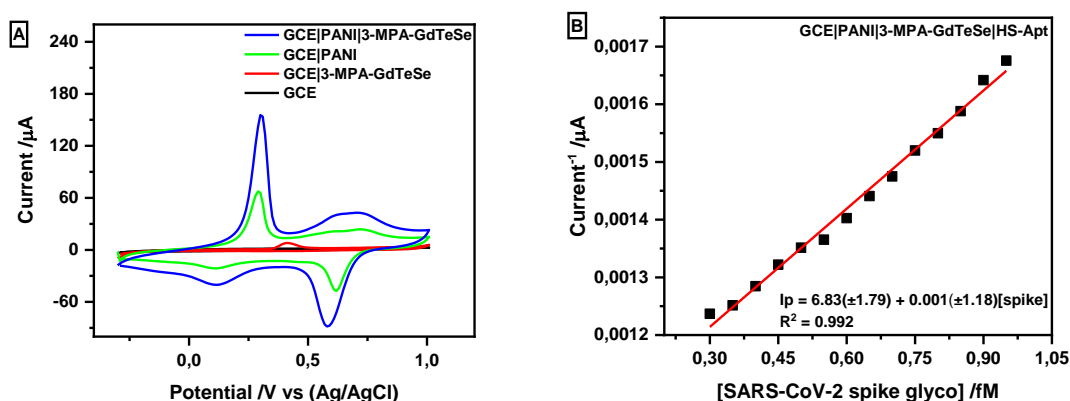

Figure 1: (a) Electro comparison of 3-MPA-GdTeSe, PANI and PANI|3-MPA-GdTeSe at the surface of GCE using CV and (b) sensitivity of HS-Apt|PANI|3-MPA-GdTeSe aptasensor for spike glycoprotein using SWV.

An electrochemical sensor for caffeine based on graphene quantum dots-manganese oxide nanocomposite modified electrode

Nyasha Midzi[a], Omotayo Arotiba[b]

[a]Department of Chemical Sciences, University of Johannesburg, Doornfontein 2028, Johannesburg, South Africa,

[b]Centre for Nanomaterials Science Research, University of Johannesburg, South Africa

E-mail: ntmidzi@gmail.com

The use of stimulants for cognitive enhancement has been on the rise as the world is changing and presses a huge demand on individuals to perform tasks (Addicott, 2014). Caffeine is a psychostimulant and it is one of most consumed in product as its sources are natural products thus it is easily accessible to the whole population in different forms (Verster, 2018). The increased risk of hypertension and cardiovascular diseases and anxiety. The traditional methods of analysis such as chromatography have short falls such as sample pre-treatment, expensive to run and require trained personnel (Amiri-Aref, 2014). An electrochemical sensor based on a glassy carbon electrode modified with graphene quantum dots and manganese dioxide nanocomposite. The GCE-GQD-MnO2 modified electrode had a 2.35 increase in current in comparison with the bare GCE. The GCE-GQD-MnO2 was used to detect caffeine in analytical and real samples in the range of 25 µM to 300 µM with a detection limit 9.175 µM.

References

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Quantitation of Nicotine in Flavored Hookah Pipe Tobacco at a Nitrogen-Doped Carbon Nanosheet/Poly(amidoamine) Dendrimer-based Electrochemical Sensor

Sesethu Makaluza[1,2], Nyasha Midzi[1,2], Foluke O.G. Olorundare[1], Dimpo S. Sipuka[1,2], Tsholofelo I. Sebokolodi[1,2], Duduzile Nkosi[1,2], Omotayo A. Arotiba*[1,2]

Corresponding author: Omotayo A. Arotiba (oarotiba@uj.ac.za)

Keywords: Electrochemical sensor; nicotine; hookah pipe tobacco; nitrogen-doped carbon nanosheet; poly(amidoamine) dendrimer

Nicotine can be a drug of abuse and the smoking of hookah pipe products may be an alternative path to ingesting harmful amounts of nicotine[1]. To show the possible danger of hookah pipe smoking to its consumer, a nitrogen-doped carbon nanosheet (N-CNS)/poly(amidoamine) dendrimer (PAMAM) nanocomposite modified electrode was prepared as a sensor for the detection of nicotine in analytical and real samples. The N-CNSs were prepared by hydrothermal method, characterized, and drop cast on a glassy carbon electrode followed by electro-deposition of PAMAM dendrimer to form the sensor (GCE/N-CNSs/PAMAM) [2]. The N-CNS/PAMAM enhanced the electrochemical performance of the electrode. The sensor achieved a nicotine detection limit of 0.09 µM in standard samples and was reproducible and repeatable. The sensor was successful in selectively detecting nicotine in two local brands of hookah pipe tobacco with a 97-110 percent recovery. The amount of nicotine detected in the hookah pipe products (0.36-0.38 mg/g) may be harmful to human health.

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In-situ fabrication of a Z-scheme Bi₂O₂S/NiTiO₃ heterojunction photoanode for the photoelectrochemical degradation of sulfamethoxazole in wastewater

Kehinde D. Jayeola[a], Omotayo A. Arotiba[b]

ᵃDepartment of Chemical Sciences, University of Johannesburg, Doornfontein 2028 Johannesburg, South Africa

ᵇCentre for Nanomaterials Science Research, University of Johannesburg, Johannesburg, 2028, South Africa

* Correspondence: oarotiba@uj.ac.za

The attempt to regulate water contamination, especially pollutants attributed to pharmaceuticals has led to the exploration into the utilisation of the photoelectrochemical (PEC) degradation process. In this work, we fabricated and characterised a Z-scheme Bi₂O₂S/NiTiO₃ heterojunction photoanode for the photoelectrochemical degradation of sulfamethoxazole in wastewater. The Bi₂O₂S/NiTiO₃ nanoparticles was synthesised via an in-situ hydrothermal method and characterised using various techniques such as XRD, FESEM, TEM, Electrochemical impedance spectroscopy, Mott Schottky, Photocurrent response, and UV-Vis Diffuse reflectance spectroscopy. The fabricated photoanode exhibited enhanced optical and photoelectrochemical properties compared to pristine Bi₂O₂S and NiTiO₃. The photoanode demonstrated efficient charge separation and suppressed recombination of photogenerated charge carriers, resulting in improved photoelectrocatalytic activity due to the strong contact between Bi₂O₂S and NiTiO₃ in the heterojunction formation. The photoelectrochemical degradation of sulfamethoxazole was investigated under different conditions, revealing the optimal current density and the synergistic effect of photocatalysis and electrochemical oxidation processes. The photoanode was found to degrade 80% of 5mg/L sulfamethoxazole in water after 180 min. The stability and reusability of the Bi₂O₂S/NiTiO₃ photoanode were also evaluated, indicating its potential for practical applications in wastewater treatment. Furthermore, the radical trapping experiments provided insights into the reactive species responsible for the degradation process. The proposed Z-scheme heterojunction formation mechanism explains the observed photoelectrocatalytic behavior of the Bi₂O₂S/NiTiO₃ photoanode. Overall, this study contributes to the development of efficient and sustainable photoanode for environmental remediation

1   Wakjira *et al.,* Bismuth-Based Z-Scheme Heterojunction Photocatalysts for Remediation of Contaminated Water. *ACS Omega.* **2024** ;9(8):8709-8729