CONCLUSIONS

AND

RECOMMENDATIONS

CONCLUSIONS

This thesis describes the electron transport and electrocatalytic properties of both electrodeposited and the chemically-synthesized metal and metal oxides MO (where M = Ni, Co, Fe) nanoparticles supported on single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT) platforms towards the electrocatalytic oxidation of important molecules such as hydrazine, diethylaminoethanethiol (DEAET), nitrite and dopamine. It has been shown that edge plane pyrolytic graphite electrodes modified with funtionalised CNTs electro-decorated with metal and metal oxide nanoparticles exhibit enhanced electrochemical response towards electro-oxidation of these analytes in aqueous buffered solution at different pH conditions where the analytes ionise maximally. The flowing results should be emphasised:

(i) SWCNT-Ni and the SWCNT-Fe modified electrodes demonstrated comparable electrochemical response towards hydrazine oxidation.

(ii) Electrochemical impedance spectroscopy study indicated that hydrazine oxidation on SWCNT-metal hybrids are rather complicated and follow electrical equivalent circuit model typical of adsorption-controlled charge transfer kinetics with some resemblance to the behaviour of electrolyte-insulator-semiconductor sensors.

(iii) This thesis provide some insights into the electrooxidative mechanism of hydrazine at carbon electrodes modified with single-walled carbon nanotubes decorated with metal and metal oxide films.

(iv) The SWCNT-Ni modified electrode showed enhanced current response towards detection of DEAET compared with other

SWCNT-M or SWCNT-MO nanocomposite modified electrodes.

(v) DEAET was detected at nano molar concentration, but the adsorptive behavior of the SWCNT-Ni may be seen as a limitation to its ultra-low detection (and very likely other related analytes) using the chronoamperometric methodology.

(vi) Synthesised M and MO nanoparticles on MWCNT platform offered less adsorptive behaviour towards hydrazine and DEAET electrooxidation compared with their counterpart electrodeposited nanocomposite on SWCNT platform.

(vii) The ability to synthesised nano-scaled metal and metal oxide nanoparticles in high commercial quantity compared to the very low and commercially unavailable nano material by electrodeposition method is one of the factors explored in this study.

(viii) MWCNT-Ni nanocomposite modified electrode yielded the fastest electron transport as well as the best electrocatalytic behaviour towards DEAET and hydrazine compared with other electrodes investigated or reported in the literature.

(ix) The enhancement is associated with high electrical-conducting MWCNTs which form a synergistic behaviour with the nickel nanoparticles.

(x) Electrocatalytic oxidation of nitrite was favoured on Co nanoparticles modified electrode.

(xi) The detection and the electro-catalytic oxidation of nitrite were successful on all the Co modified electrodes investigated.

(xii) EPPGE-SWCNT-Co electrode made by electrodeposition has the fastest electron transport towards nitrite compared with other Co modified electrodes.

(xiii) Attempts to use CNTs as supports for synthesised Co and Co_3O_4 nanoparticles did not improve the electrochemistry of nitrite, a further advantage of the synthesis method over the electrodeposited counterparts that require CNTs.

(xiv) The electrocatalytic-oxidation of nitrite on the electrodes followed adsorption-controlled electrochemical process with complex impedance behaviour.

(xv) Electrocatalytic detection of DA was best at electrode modified by both electrodeposited and synthesised Fe_2O_3 nanoparticle catalyst supported on CNT platform.

(xvi) From EIS, the pseudo-capacitive nature of the Fe_2O_3 modified electrodes is a function of their electrochemical stability towards DA.

(xvii) Analysis of DA at these electrodes showed that DA oxidation proceeded through diffusion and surface controlled electrochemical process.

(xviii) The limit of detection (LoD), catalytic rate constant (k) of the electrodes, and the diffusion coefficient (D) of DA agreed favourably with values reported earlier in literature.

(xix) The CNT-Fe_2O_3 modified electrodes clearly separated DA signal from the interfering effect of AA even at AA concentration of 50-100 folds that of DA.

(xx) The electrodes have also proven to be a potential sensor for dopamine detection in real sample analysis.

(xxi) Electrocatalytic oxidation of the four analytes (DEAET, hydrazine, nitrite and dopamine) was successful on EPPGE-

SWCNT-PB modified electrode in terms of current response and on-set potential for catalysis compared with the bare EPPGE.

(xxii) The analytes oxidation current response increases with increasing PB layer on the electrode making EPPGE-SWCNT-3PB the best electrode. This electrode has the fastest electron transport and lowest R_{ct} towards the analytes electrocatalysis.

(xxiii) DA oxidation on the EPPGE-SWCNT-3PB proceeds via diffusion-controlled process while DEAET, hydrazine and nitrite oxidation was affected by some degree of adsorption of the reaction intermediates as indicated by their Tafel slopes and the standard free energy change due to adsorption.

(xxiv) The sensitivities, linear concentration ranges, and detection limits of these analytes on the EPPGE-SWCNT-3PB electrode agreed favourably and even better than values reported in the literature.

(xxv) The EPPGE-SWCNT-3PB electrode detects DA even at AA concentration which is 1000 times that of DA, with a wide potential separation of about 200 mV.

(xxvi) The electrode is electrochemically stable, re-usable and can be used for the analysis of DA in real drug samples with satisfactory accuracy and reproducibility.

(xxvii) The CNT-MO nanocomposite modified electrodes were screened for their supercapacitive properties.

(xxviii) SWCNT-NiO nanocomposite modified electrode exhibits remarkable supercapacitive behaviour in neutral and acidic

media compared to SWCNT-Fe_2O_3 and SWCNT-Co_3O_4 counterparts.

(xxix) The capacitive behaviour of the SWCNT-NiO was more enhanced in a H_2SO_4 solution than the Na_2SO_4 electrolyte, possibly due to the high conductivity of the former.

(xxx) EIS study indicated that the electrolyte ions could penetrate more easily into the pores of the BPPGE-SWCNT-NiO electrode at a reasonable frequency range.

(xxxi) SWCNT-NiO electrode maintained good stability with only about 5% loss of its specific capacitance after 1000 cycle life.

RECOMMENDATIONS

(1) This work recommends and cautions researchers who wish to use this emerging type of CNT-metal nanoparticle electrocatalytic / sensing platform to first establish the adsorption phenomenon with a view to understanding and applying the most appropriate electrochemical technique to be used for reliable analytical parameters.

(2) The adsorption phenomenon should be subject of future concern more importantly, in reducing the effect on the limit of detection of the fabricated sensors.

(3) Large scale fabrication of the sensors for industrial application in food, agriculture, pharmaceuticals, military, and forensic use should be maximised.

(4) The CNT-MO nanocomposite materials have also demonstrated some potential that needs to be further explored for future application in energy generating and storing devices such as batteries and suoercapacitors.

APPENDIX A

List of publications in peer-reviewed journals from this thesis

1. **Abolanle S. Adekunle**, Bolade O. Agboola, Jeseelan. Pillay, Kenneth I. Ozoemena, Electrocatalytic detection of dopamine at single-walled carbon nanotubes-iron (III) oxide nanoparticles platform, *Sens. Actuator: Chemical B* 148 (2010) 93-102.

2. **Abolanle S. Adekunle**, Jeseelan Pillay, Kenneth I. Ozoemena, Probing the electrochemical behaviour of SWCNT-Cobalt nanoparticles and their electrocatalytic activities towards the detection of nitrite at acidic and physiological pH conditions, *Electrochim. Acta* 55 (2010) 4319-4327.

3. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, Electrocatalytic Oxidation of hydrazine and diethylaminoethanethiol at Single-walled carbon nanotubes / Prussian Blue Nanoparticles Modified Electrode, *Electroanalysis* 22 (2010), 2519-2528

4. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, Electron transport and electrocatalytic properties of MWCNT/nickel nanocomposites: Hydrazine and Diethylaminoethanethiol as analytical probes, *J. Electroanal.l Chem.* 645 (2010) 41-49.

5. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, Comparative surface electrochemistry of Co and Co_3O_4 nanoparticles: Nitrite as an analytical probe, *Int. J. Electrochem.* 5 (2010) 1972-1983.

6. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, Voltammetric and impedimetric properties of nano-scaled γ-Fe_2O_3 catalysts supported on multi-walled carbon nanotubes: catalytic detection of dopamine, *Int. J. Electrochem. Sci.* 5 (2010) 1726-1742.

7. **Adekunle A. S.**, Pillay J., Ozoemena K. I., Electrocatalytic detection of V-type nerve agent on SWCNT/Ni modified electrode: Adsorption controlled process, *Electroanalysis*, 20 (2008) 2587-2591.

8. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, Electron transfer behaviour of single-walled carbon nanotubes electro-decorated with nickel and nickel oxide layers. *Electrochim. Acta* 53 (2008) 5774-5782.

9. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, Insights into the electro-oxidation of hydrazine at single-walled carbon-nanotube-modified edge-plane pyrolytic graphite electrodes electro-decorated with metal and metal oxide film, *J. Solid State Electrochem*. 12 (2008) 1325–1336.

10. **Abolanle S. Adekunle**, Jeseelan Pillay, Kenneth I. Ozoemena, Electrocatalytic properties of prussian blue nanoparticles supported on poly(m-aminobenzenesulfonic acid) – functionalized single-walled carbon nanotubes toward the detection of dopamine, (Submitted).

11. **Abolanle S. Adekunle,** Kenneth I. Ozoemena, Electrosynthesised metal (Ni, Fe, Co) oxide films on single-walled carbon nanotube platforms and their supercapacitance in acidic and neutral pH media, *Electroanalysis* (In-press).

12. **Abolanle S. Adekunle**, Kenneth I. Ozoemena, MWCNTs/Metal (Ni, Fe, Co) oxide nanocomposites as potential material for supercapacitors application in acidic and neutral media, *J. Power Sources* (Submitted).

APPENDIX B

List of conference Presentations from this thesis.

1. "Synthesis, characterization and the Electrocatalytic Properties of Prussian blue/Single-walled Carbon Nanotubes Composites" Adekunle A. Saheed, Abdullahi M. Farah and Kenneth I. Ozoemena, NanoAfrica 2009 International Conference on NanoScience and Nanotechnology, CSIR International Convention Centre Pretoria,South Africa, February 1-4, 2009 (**ORAL PRESENTATION BY A.S. ADEKUNLE**).

2. "Metal-Decorated Single Walled Carbon Nanotubes in Elctrocatalysis" A.S. Adekunle and K.I. Ozoemena, International (SA-UK research Network)Workshop on Electrochemistry for Nanotechnology, CSIR Intrnational Convention Centre, Pretoria, South Africa, April 9-10, 2008 (**ORAL PRESENTATION BY A.S. ADEKUNLE**).

3. "Electron Transport and Electrocatalytic Properties of Nickel Nanoparticle-Electrodecorated Single-Walled Carbon nanotubes" Adekunle Abolanle S. and Kenneth I Ozoemena, 1st International Symposium on Electrochemistry ElectrochemSA, University of Western cape, Belville, Cape Town, South Africa, July 9-11, 2008 (**POSTER PRESENTATION BY A.S. ADEKUNLE**).

4. "Electrodecorated Single-Walled Carbon Nanotubes Metal Nanoparticles Composite in Electrocatalysis" Adekunle Abolanle S. and Kenneth I. Ozoemena, 1st Annual DST/MINTEK Nanotechnology Innovation Centre Sensor Workshop, Rhodes University, Grahamstown,South Africa, September 11-12, 2008 (**ORAL PRESENTATION BY A.S. ADEKUNLE**).

5. "Synthesis and Electrocatalysis of Metal Nanoparticles-Decorated Carbon Nanotubes" Adekunle Abolanle S and Kenneth I. Ozoemena, 39th National Convention of the South Africa Chemical Institute (SACI), Stellenbotch University, South Africa, 30 Nov. – 5 Dec. 2008 (**ORAL PRESENTATION BY A.S. ADEKUNLE**).

6. "Electrocatalytic Oxidation of Chemical Warfare Agents at Edge Plane Pyrolytic Graphite Electrodes Decorated with Single-walled Carbon Nanotubes and Nickel Nanoparticles" Abolanle S. Adekunle and Kenneth I. Ozoemena, The South African Chemical Institute Young Spectroscopists' Symposium, Film Auditorium, University of South Africa, Pretoria, South Africa 10 October, 2007 (**ORAL PRESENTATION BY A.S. ADEKUNLE**).

7. "Nano-Architectures and Nanoparticles Incorporating Carbon Nanotubes and Fullerenes: New Hybrids with Excellent Electron Transports " Kenneth I. Ozoemena, and Duduzile Nkosi, Jeseelan Pillay, Abolanle S Adekunle, Alfred Mocheko, Solomon Mamuru, Bolade Agboola. SACI, INORG 007, Langebaan, Cape Town, July 8-12, 2007.