CONCLUSION

AND

RECOMMENDATIONS

CONCLUSION

This dissertation essentially describes the electrocatalytic properties of MPCAuNP, SWCNT-PABS and MPCAuNP, SWCNT-PABS functionalized with ironphthalocyanine complexes on gold electrode electrode towards the detection of hydrogen peroxide and epinephrine. The following important results obtained in this work should be emphasised:

- The electrochemical properties of DMAET SAM, with and without integration with SWCNT-PABS were probed for the first time. SWCNT-PABS was found to be irreversibly attached to the DMAET.
    - Electric field-induced protonation/deprotonation of the DMAET head group ($-N(H)^{+}(CH_3)_2$) resulted in the well-defined reversible voltammetry observed for DMAET SAM.
    - The surface pK_a of DMAET was examined for the first time and its value of ~7.6 was found to be ~3 pK_a units less than its solution pK_a.
- The integration of SWCNT-PABS and nanoparticles of redox-active FePc complex via electrostatic layer-by-layer assembly on Au-DMAET were explored for the first time.
    - The electron transfer kinetics of the ferricyaninde/ferrocyanide redox probe decreased with added alternating layers of SWCNT-PABS and nanoparticles of FePc.

Conclusion.....

- The reduction rate of hydrogen peroxide increased with added alternating layers of SWCNT-PABS and nanoparticles of FePc.
- DMAET-SWCNT-PABS SAM proved to be more efficient in epinephrine detection than the layer-by-layer nano-architectural assembly.

- The combined integration of FeTSPc complex and SWCNT-PABS investigated for the first time.
  - The nano-thin films of the combined redox-active species exhibited excellent electrochemical stability and showed faster electron transport in $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox probe compared to the individual FeTSPc and SWCNT-PABS.
  - The combined species also showed enhanced detection towards epinephrine.
- The solid films exhibited excellent electrochemical stability. The SWCNT-PABS acts as efficient conducting species in the mixed hybrids (Au-DMAET-SWCNT-PABS/FeTSPc) thus facilitating electron transport between the integrated FeTSPc and the underlying gold substrate.
- For the first time the electron transfer dynamics of surface-confined gold nanoparticles involving different ratios of carboxylated- and hydroxyl-containing ligands has been fabricated and described.

Conclusion.....

- In both aqueous and nonaqueous solutions, there is electronic communication between the immobilized MPCAuNPs and the gold electrode, possibly from electron tunneling between these protecting ligands and the gold electrode.
- the electronic communication is strongly influenced by the hydrophilicity of the head groups (-OH and -COOH); in aqueous solution the electron transport of the –COOH based ligand is favoured, while in the nonaqueous medium the electron transport of the -OH based ligands is favoured.
- Au-DMAET-MPCAuNP-$COOH_{99\%}$ showed an excellent suppression of the voltammetric response of the ascorbic acid and an enhanced electrocatalytic activity towards the detection of epinephrine compared to other MPCAuNPs studied.
- Simply put, this study has provided some useful physical insights into the impact of different ratios of the protecting –OH and –COOH based monolayer ligands of redox-active gold nanoparticles on the dynamics of electron transport between solution species, in organic and aqueous media, and the electrode surface.

RECOMMENDATIONS

- The amplification of the electrochemical response to H_2O_2 detection suggests that this type of electrode could provide an important nano-architectural sensing platform for biosensor development.
- The extent to which the ratios of protecting ligands in MPCAuNP influence electron transport is crucial for the potential applications of such platforms in many areas such as in molecular electronics as well as chemical and biological sensing.
- Integration of *nano*FePc and MPCAuNP for the detection of H_2O_2.
- The use of HRP and Cyt C instead of FePc complexes for MPCAuNP studies.
- Other analytes and neurotoxins can be investigated using the modified electrodes.
- Interchange the order of the attached species in the assembly strategy by using charges opposite to that used in this work.
- Use of a negatively charged base monolayer.

It is envisaged that the results shown in this dissertation should provide some thoughts on the factors that should be considered when designing molecular-scale electronics or electrocatalytic sensing devices that employ these materials, and possibly for some other redox-active metal nanoparticles.

APPENDIX A: PEER-REVIEWED ARTICLES RELATED:

(a) DIRECTLY TO THIS DISSERTATION:

1. **J. Pillay**, B. O. Agboola, K. I. Ozoemena, Layer-by-layer self-assembled nanostructured phthalocyaninatoiron(II) / SWCNT-*poly*(*m*-aminobenzene sulfonic acid) hybrid system on gold surface: Electron transfer dynamics and amplification of H_2O_2 response", *Electrochem. Commun.* 11 (2009) 1292.
2. **J. Pillay**, K.I. Ozoemena, Electrochemistry of 2-dimethylaminoethanethiol SAM on gold electrode: Interaction with SWCNT-poly(*m*-aminobenzene sulphonic acid), electric field-induced protonation-deprotonation, and surface pK_a", *Electrochim. Acta* 54 (2009) 5053.
3. **J. Pillay**, K.I. Ozoemena, T.R. Tshikhudo, "Monolayer-Protected Gold Nanoparticles: Impacts of Stabilizing Ligands on the Heterogeneous Electron Transfer Dynamics and Voltammetric Detection", *Langmuir* (2010) DOI: 10.1021/la904463g
4. B.O. Agboola, **J. Pillay**, K. Makgopa, K.I. Ozoemena, "Cyclic voltammetric and impedimetric properties of mixed self-assembled nanothin films of water-soluble SWCNT-*poly*(*m*-aminobenzene sulfonic acid) and iron (II) tetra-sulphophthalocyanine at gold electrode", Submitted to *Thin Solid Films*.

5. **J. Pillay**, K.I. Ozoemena, "Electron transport and voltammetric detection properties of gold nanoparticle-nanosized iron (II) phthalocyanine bilayer films", in preparation.

(b) INDIRECTLY TO THIS DISSERTATION:

1. A.S. Adekunle, **J. Pillay**, K. I. Ozoemena, "Electrocatalysis of 2-Diethylaminoethanethiol at Nickel Nanoparticle-Electrodecorated Single-Walled Carbon Nanotube Platform: An Adsorption-Controlled Electrode Process", *Electroanalysis* 20 (2008) 2587.
2. K. I. Ozoemena, D. Nkosi, **J. Pillay**, "Influence of solution pH on the electron transport of the self-assembled nanoarrays of single-walled carbon nanotube-cobalttetra-aminophthalocyanine on gold electrodes: Electrocatalytic detection of epinephrine", *Electrochimica Acta* 53 (2008) 2844.
3. B. O. Agboola, A. Mocheko, **J. Pillay** and K. I. Ozoemena, "Nanostructured cobalt phthalocyanine single-walled carbon nanotube platform: electron transport and electrocatalytic activity on epinephrine", *Journal of Porphyrins and Phthalocyanines* 12 (2008) 1289.
4. N.S. Mathebula, **J. Pillay**, G. Toschi, J.A. Verschoor, K.I. Ozoemena, "Recognition of anti-mycolic acid antibody at self-assembled mycolic acid antigens on a gold electrode: a potential

impedimetric immunosensing platform for active tuberculosis" *Chem. Comm.* 23 (2009) 3345.

5. A.S. Adekunle, **J. Pillay**, K.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", *Electrochimica Acta* (2008), doi:10.1016/j.electacta. 2009.02.102.
6. D. Nkosi, **J. Pillay**, K.I. Ozoemena, K, Nouneh, M. Oyamac, "Heterogeneous electron transfer kinetics and electrocatalytic behaviour of mixed self-assembled ferrocenes and SWCNTs layers", *Physical Chemistry Chemical Physics* (2009) DOI: 10.1039/b00000.
7. K.I. Ozoemena, N.S. Mathebula, **J. Pillay**, G. Toschi, J.A. Verschoor, "Electron transfer dynamics across self-assembled N-(2-mercaptoethyl) octadecanamide/ mycolic acid layers: impedimetric insights into the structural integrity and interaction with anti-mycolic acid antibodies", *Physical Chemistry Chemical Physics* (2009) DOI: 10.1039/b915930d.
8. A.S. Adekunle, B.O. Agboola, **J. Pillay**, K.I. Ozoemena, "Electrocatalytic detection of dopamine at SWCNT/Fe_2O_3 nanoparticle platform", submitted to *Sensors and Actuators B*.

APPENDIX B: LIST OF CONFERENCE PRESENTATIONS RELATED DIRECTLY TO THIS DISSERTATION:

1. "Monolayer-Protected Gold Nanoclusters as a Platform for the Development of High-Performance Electrochemical Biosensors", Jeseelan Pillay and Kenneth I. Ozoemena, International SA-UK Research Network on Electrochemistry for Nanotechnology, CSIR International Convention Centre, Pretoria, SOUTH AFRICA, April 9 – 10,2008 (**ORAL PRESENTATION BY J. PILLAY**).

2. Jeseelan Pillay, NRF South African PhD Project Conference, Emperor's Palace, Kemton Park, Guateng, SOUTH AFRICA, May 25 – 27, 2008. 1 of 300 Invited Delegates.

3. "Layer-by-Layer Self Assembled Nano-Architectural Platform of SWCNT-nanoFePc: Characterization and Electrocatalysis", Jeseelan Pillay and Kenneth I. Ozoemena, 1st International Symposium on Electrochemistry, ElectrochemSA, University of Western Cape, Cape Town, SOUTH AFRICA, July 9 – 11, 2008 (**ORAL PRESENTATION BY J. PILLAY**).

4. "Electrocatalytic and Sensing Platforms based on Molecular and Nanomaterials", Jeseelan Pillay and Kenneth I. Ozoemena, University of Pretoria Chemistry Department 2008 Research Day, University of Pretoria, Pretoria, SOUTH AFRICA, July 21, 2008 (**ORAL PRESENTATION BY J. PILLAY**).

5. "Biosensing Platform based on LBL Networks incorporating Enzyme and Nanomaterial", Jeseelan Pillay and Kenneth I.

Ozoemena, 39th National Convention of the South African Chemical Institute, Stellenbosch University, Stellenbosch, SOUTH AFRICA, November 30 – December 5, 2008 (**ORAL PRESENTATION BY J. PILLAY**).

6. "Self-Assembled Layer-by-Layer Networks Incorporating Single-Walled Carbon Nanotubes and Iron Phthalocyanine", Jeseelan Pillay and Kenneth I. Ozoemena, Nanomaterials Conference, Ocean Maya, Playa del Carmen, MEXICO, December 7 – 10, 2008 (**POSTER PRESENTATION BY J. PILLAY**).

7. "Electron Transfer and Electrocatalysis of Self- Assembled Films of Monolayer-Protected Clusters of Gold Nanoparticles", Jeseelan Pillay and Kenneth I. Ozoemena, International Conference on Nanoscience and Nanotechnology, CSIR International Convention Centre, South Africa, 1 – 4 February, 2009 (**ORAL PRESENTATION BY J. PILLAY**).

8. "Architecture of monolayer protected clusters of gold nanoparticles containing different ligand composition on gold electrodes", Jeseelan Pillay, Kenneth I. Ozoemena, T.R. Tshikhudo, DST/Mintek annual NIC "Nanotechnology for Development" Workshop, Council Chambers, Kingsway Campus, Auckland Park, University of Johannesburg, 24 – 25 September, 2009 (**ORAL PRESENTATION BY J. PILLAY**).