CONCLUSIONS AND FUTURE PERSPECTIVE

The remarkable electrochemical and electrocatalytic activities of the studied organometallic complexes (FePc and Fc complexes) has been described in this work. The construction by sequential self-assembly process of a reproducible and stable redox-active nanostructured arrays of single-walled carbon nanotube (SWCNT) coordinated to organometallic complexes on a gold surface was successfully developed.

A number or remarkable findings in this work should be emphasized; first, this represents the first report on the coordination by self-assembly of a redox-active iron phthalocyanine complex to surface-confined SWCNT via ester bond formation. Second, the redox properties of the SAMs exhibit strong dependence on the reaction of the head groups and the pH of the working electrolytes. Third, Au-Cys-SWCNT-FeOHETPc electrode showed much faster electron transfer kinetics compared to the Au-Cys-SWCNT-CoTAPc electrode. Fourthly, the high electron transfer capability of the Au-Cys-SWCNT-FeOHETPc electrode over the Au-Cys-SWCNT or the Au-Cys-FeOHETPc or the Au-FeOHETPc electrodes confirms that SWCNT greatly improves the electronic communication between FeOHETPc and the bare gold electrode. Finally, our results clearly showed that aligned SWCNT-FeOHETPc arrays exhibit much faster electron transfer kinetics to

redox-active species in solutions compared to the randomly dispersed (drop-dried) SWCNT electrode. The advantageous electron transfer properties of the Au-Cys-SWCNT-FeOHETPc electrode, coupled with its ease of fabrication and chemical stability, could be found useful in electrochemical sensing and catalysis, and such possibilities would form the main subjects of future studies**.** These findings could also apply to iron phthalocyanine related complexes, notably the iron porphyrins and Schiff bases. This implies the impact of peripheral substituents has on the phthalocyanine core towards electrocatalytic behaviour.

The electrocatalytic activity of a coordination self-assembled SWCNT-FeOHETPc hybrid on gold electrode show that this hybrid exhibit greater senstivity towards the detection of thiocyanate compared to electrodes containing SWCNT or FeTAPc or FeOHETPc only, confirming the ability of the SWCNTs to function as effective conductive nanowires.

Cyclic voltammetric and impedance spectroscopic characteristics of the redox-active SAMs revealed reversible electrochemistry in aqueous solutions with different electron-transfer rates. Preliminary electrocatalytic investigation proved that both SAMs exhibit comparable electrocatalytic responses towards the detection of dopamine in pH 7.4 PBS. This proposed electrode fabrication technique

is unique; it can be used for fundamental studies of the electron transfer processes of surface confined metalloporphyrin and metallophthalocyanimne complexes and, importantly, it promises to provide an opportunity for controlled fabrication of stable organometallic sensing platforms. For example, further studies to explore other electrocatalytic properties (e.g., influence of surface charges to electron transfer) and sensing capabilities of this type of MPc-SAM to organic analytes will constitute the some of the subjects of future investigations.

The electrochemistry of electron transfer dynamics of ferrocene-terminated self-assembled monolayers (SAMs), co-adsorbed with SWCNTs on gold electrode, have been interrogated for the first time. Factors influencing electron transport within organized molecular assemblies are crucial for the potential applications of such platforms in many areas such as in molecular electronics, chemical and biological sensings. The important findings in this work should be emphasized. First, the neighbouring SWCNTs in the ferrocene molecular assemblies exert distinct impacts on the global electron transport and electroacatalytic behaviour of the ferrocenes. Second, that the presence of SWCNTs in the ferrocene assembly synergistically enhances the electrocatalytic detection of thiocyanate compared to the ferrocene or SWCNTs alone. In a

nutshell, this work has provided some useful physical insights into the impact of local SWCNTs microenvironment surrounding a redox-active and electocatalytic molecule (not only ferrocene but other related organometallic species) on the dynamics of electron transport between solution species and electrode. We envisage that these insights have provided some thoughts on the factors that must be considered when designing molecular-scale electronics or electrocatalytic devices that employ CNT and ferrocenes (or related species). Future work on these newly developed findings should include the application as electrocatalysts for sensing biological molecules such as dopamine and epinephrine.

APPENDIX A

Publications in peer-reviewed journals form this Thesis

1. **D. Nkosi**, K. I. Ozoemena, "Self-assembled nano-arrays of single-walled carbon nanotubes octa(hydroxyethylthio) phthalocyaninatoiron(II) on gold surfaces: Impacts of SWCNT and solution pH on electron transfer kinetics" *Electrochim. Acta,* 53, 2008, 2782-2793.

2. **D. Nkosi**, K. I. Ozoemena, "Interrogating the electrocatalytic properties of coordination self-assembled nanostructures of single-walled carbon nanotube–octa(hydroxyethylthio) phthalocyaninatoiron(II) using thiocyanate as an analytical probe" *J. Electroanal. chem.*, 621,2008,304-313.

3. 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-Cobalt tetraaminophthalocyanine on gold electrodes: Electrocatalytic detection of epinephrine" *Electrochim. Acta,* 53, 2008, 2844-2851.

4. K.I. Ozoemena, T. Nyokong, **D. Nkosi**, I. Chambrier, and M.J. Cook, "Insights into the Surface and Redox Properties of Single-Walled Carbon Nanotube–Cobalt(II) tetra-aminophthalocyanine Self-Assembled on Gold Electrode", *Electrochim. Acta* 2007, 52, 4132-4143.

5. **D. Nkosi**, J. Pillay, K. I. Ozoemena, K. Nouneh, M. Oyama, Heterogeneous electron transfer kinetics and electrocatalytic behaviour of mixed self-assembled ferrocenes and SWCNTs layers Phys. Chem. Chem. Phys. 2010, 12, 604-613.

APPENDIX B

List of Conference Presentations from this Thesis

1. "*Self-Assembled Nanostructures of Iron-Phthalocyanines and Mixed Monolayers of Single-Walled Carbon Nanotubes.*" **Duduzile Nkosi** and Kenneth I. Ozoemena CSIR International Convention Centre, Pretoria, South Africa february 1-4, 2009 (Oral presentation)

2. "*Electrochemical Activity of Self-Assembled Mixed Monolayers of Single-Walled Carbon Nanotubes and Ferrocenes on Gold Electrode".* **Duduzile Nkosi** and Kenneth I. Ozoemena, Nanometerial Conference, Playa del Carmen, Cancun, Mexico, December 3-8, 2008 (poster presentation)

3. "*Catalytic Activities of Self-Assembled Nanostructures of Iron-phthalocyanines and Ferrocene-Single-Walled Carbon Nanotubes*" **Duduzile Nkosi** and Kenneth I. Ozoemena, ECSA, 1st international symposium on electrochemistry, Bellville, Cape Town, July 8-11, 2008. (Oral presentation)

4. *"Self-Assembled Nanostructures of Iron- Phthalocyanines and Ferrocenes as Sensing platforms"* **Dudu Nkosi** and Kenneth I. Ozoemena International (SA-UK Research Network) workshop on electrochemistry for nanothechnology, CSIR, Pretoria, April 9-10, 2008. (Oral presentation)

5. "*Electron transfer at Gold Electrodes Modified with Self-Assembled Monolayers of Carbon Nanotube-Iron Phthalocyanine Complex"*, **Dudu Nkosi** and Kenneth I. Ozoemena, 38th Convention of the South African Chemical Institute, Durban, SOUTH AFRICA, December 3-8, 2006. (Award winning poster presented by D. Nkosi)