

**Electrochemical and electrocatalytic properties of
iron(II) and cobalt(II) phthalocyanine complexes
integrated with multi-walled carbon nanotubes**

by

SOLOMON ALMANTO MAMURU

A dissertation submitted in fulfilment of the

requirements for the degree

of

DOCTOR OF PHILOSOPHY

in the Faculty of Natural and Agricultural Science

University of Pretoria

October, 2010

Supervisor: Dr KI Ozoemena



DEDICATION

This dissertation is dedicated to my wife Fidelia and two children, Sheni
Adrian and Bonoshi Benedicta for their patience and understanding.

DECLARATION

I declare that the thesis hereby submitted to the University of Pretoria for the degree of Doctor of Philosophy has not been previously submitted by me for a degree at any other University, that it is my own work in design and execution, and that all material contained therein has been duly acknowledged.

Solomon Asmanto Mamuru.....

ACKNOWLEDGEMENTS

I wish to express my sincere and profound gratitude to the Almighty father for His guidance, blessing and protection throughout the duration of my study in South Africa. To Prof. Jacob K. Kwaga and the management of Adamawa State University, Mubi for the opportunity given me to study outside the shores of Nigeria, I say thank you. Sincere appreciation to my supervisor, Dr (Prof.) Kenneth I. Ozoemena, who out of his valuable time read through and made necessary corrections, also not forgetting his moral, financial support and harsh criticism; you have made a diamond out of coal. To the staff and members of Chemistry Department, University of Pretoria and the National Research Foundation (NRF) for the prestigious nanoflagship bursary, I am grateful. To my family, especially my mother Catherine Abubakar, my sister Celina Kanmodi, and my brothers Henry and Tunde, for their moral support and encouragement; to all the members of our research group, we had a wonderful time, despite all inconveniences. I am ever grateful to my very good South African friends, Tebogo Mogosoana and Refilwe Mokate; you made my stay in South Africa worthwhile. I will miss you guys. Finally, to all the friends I made while in South Africa, who have in one way or another impacted positively to my stay in South Africa; especially Pius Chin, Esme, Essien, Sello Segoa, and all the staff of the international student division.

ABSTRACT

For the first time, new metallophthalocyanine (MPc) complexes: (i) nanostructured MPc (nanoMPc, where M = iron or cobalt); (ii) octabutylsulphonylphthalocyanine (MOBSPc, where M = iron or cobalt); and (iii) iron (II) tetrakis(diaquaplatinum)octacarboxyphthalocyanine (PtFeOCPC) were synthesized and characterized using advanced microscopic and spectroscopic techniques such as MS, AFM, HRTEM, FESEM, and EDX. Electrochemical techniques such as cyclic voltammetry, square wave voltammetry, chronoamperometry, rotating disk electrode, and electrochemical impedance spectroscopy, were used to explore the redox chemistry, heterogeneous electron transfer kinetics (HET), and electrocatalytic properties of these MPc complexes towards oxygen reduction reaction (ORR), oxidation of formic acid, thiocyanate and nitrite on a edge plane pyrolytic graphite electrode (EPPGE) platform pre-modified with or without acid functionalized multi-walled carbon nanotubes (MWCNTs). The MWCNT-MPc platforms exhibit enhanced electrochemical response in terms of (i) HET towards an outer-sphere redox probe ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$), and (ii) catalytic activities towards the investigated analytes. The MWCNT-nanoMPc electrode exhibits faster HET constant ($k_{\text{app}} \approx 30 - 56 \times 10^{-2} \text{ cms}^{-1}$) compared to their bulk MPc counterparts ($\approx 4 - 25 \times 10^{-2} \text{ cms}^{-1}$). The MWCNT-nanoMPc exhibited enhanced electrocatalytic properties (in terms of sensitivity and limit of detection, LoD) towards the detection of thiocyanate and nitrite in aqueous solutions. ORR was a 4-

electron process with very low onset potential (-5 mV vs. Ag|AgCl saturated KCl). HET and ORR at MOBSPc complexes supported on MWCNTs showed that the MWCNT-MOBSPc exhibited larger Faradaic current responses than the electrodes without MWCNTs. The rate constant at the MWCNT-MOBSPc electrodes ($k_{app} \approx (22 - 37) \times 10^{-2} \text{ cms}^{-1}$) is about a magnitude higher than the electrodes without MWCNT ($k_{app} \approx (0.2 - 93) \times 10^{-3} \text{ cms}^{-1}$). The MWCNT-FeOBSPc electrode gave the best ORR activity involving a direct 4-electron mechanism with low onset potential (0.0 mV vs. Ag|AgCl saturated KCl). The onset potential is comparable and even much lower than recent reports. The HET and electrocatalytic properties of PtFeOCPC supported on a MWCNT platform (MWCNT-PtFeOCPC) gave enhanced electrochemical response in terms of (i) HET ($k_{app} \approx 78 \times 10^{-2} \text{ cms}^{-1}$), (ii) catalytic rate constant ($k_{cat} \approx 41 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and (iii) tolerance towards CO poisoning during formic acid oxidation. The ORR activity is a direct 4-electron transfer process at a rate constant of $2.78 \times 10^{-2} \text{ cms}^{-1}$; with a very low onset potential approximately 0.0 mV vs. Ag|AgCl saturated KCl. The electro-oxidation of formic acid at MWCNT-PtFeOCPC follows the preferred 'direct pathway'. This work clearly proves that the MWCNT-MPCs hybrid exhibit enhanced electrochemical and electrocatalytic activities towards the selected analytes compared to the MPCs alone. Considering the ease of fabrication of these electrodes (drop-dry method), these nanocomposite materials are promising platform for potential application in sensing and cataly

Table of Contents

DEDICATION	i
DECLARATION	ii
ACKNOWLEDGEMENTS.....	iii
ABSTRACT	iv
Table of Contents	vi
Abbreviations	xiv
List of Symbols	xvi
List of Schemes	xviii
List of Tables	xix
List of Figures.....	xx
CHAPTER 1	
General Overview of Dissertation	1
1.1 Background of Project.....	2
1.1.1 <i>Introduction</i>	2
1.1.2 <i>Aim</i>	3
1.1.3 <i>Objectives.....</i>	4
1.1.4 <i>Scientific novelty of the work.....</i>	4
1.1.5 <i>Publication of the work</i>	5
1.1.6 <i>Structure of the thesis.....</i>	5
References.....	6

SECTION A

CHAPTER 2

Introduction	8
2.1 Electrochemistry: An Overview	9
2.1.1. <i>Basic concepts</i>	9
2.1.1.1. <i>The electrode-solution interface</i>	10
2.1.1.2. <i>Faradaic and non-Faradaic processes</i>	13
2.1.1.3. <i>Mass transport processes</i>	14
2.1.2. <i>Voltammetry</i>	16
2.1.2.1. <i>Cyclic voltammetry</i>	17
1.1.2.1.1. <i>Reversibility</i>	18
1.1.2.1.2. <i>Irreversibility</i>	21
1.1.2.1.3. <i>Quasi-reversibility</i>	22
2.1.2.2. <i>Linear sweep voltammetry</i>	25
2.1.2.3. <i>Square wave voltammetry</i>	26
2.1.2.4. <i>Chronoamperometry</i>	29
2.1.2.5. <i>Chronocoulometry</i>	30
2.1.3. <i>Electrocatalysis</i>	32
2.1.4. <i>Electrochemical Impedance Spectroscopy</i>	34
2.1.4.1. <i>Data Presentation</i>	36
2.1.4.2. <i>Data Interpretation</i>	38
2.1.4.3. <i>Validation of Measurement</i>	40

2.2	Chemically Modified Electrodes	43
2.2.1.	<i>General Methods of Modifying Electrode Surfaces.....</i>	43
2.2.1.1.	<i>Chemisorption</i>	43
2.2.1.2.	<i>Covalent Bonding.....</i>	44
2.2.1.3.	<i>Composite.....</i>	44
2.2.1.4.	<i>Coating by thin films</i>	44
2.3	Carbon Electrodes	47
2.3.1.	<i>Diamond Electrode</i>	47
2.3.2.	<i>Graphite Electrode</i>	47
2.4	Carbon Nanotubes: General Introduction.....	54
2.4.1.	<i>Historical Perspective</i>	54
2.4.2.	<i>Structure of Carbon Nanotubes.....</i>	55
2.4.3.	<i>Synthesis of Carbon Nanotubes</i>	58
2.4.4.	<i>General Applications of Carbon Nanotubes</i>	59
2.5	Metallophthalocyanines: General Introduction.....	61
2.5.1.	<i>Historical Perspective</i>	61
2.5.2.	<i>Structure of Metallophthalocyanines</i>	61
2.5.3.	<i>Synthesis of Metallophthalocyanines.....</i>	62
2.5.4.	<i>Electronic Absorption Spectra of Metallophthalocyanines .</i>	66
2.5.5.	<i>Electrochemical Properties of Metallophthalocyanines</i>	68
2.5.5.1.	<i>Ring Process.....</i>	68
2.5.5.2.	<i>Metal Process</i>	69
2.5.6.	<i>General Applications of Metallophthalocyanines.....</i>	70

2.6	Overview of Target Analytes	72
2.6.1.	<i>Oxygen Reduction Reaction (ORR)</i>	72
2.6.2.	<i>Formic Acid Oxidation</i>	76
2.6.3.	<i>Thiocyanate Oxidation</i>	78
2.6.4.	<i>Nitrite Oxidation</i>	79
2.7	Microscopic and Spectroscopic Techniques	81
2.7.1.	<i>Atomic Force Microscopy (AFM)</i>	81
2.7.2.	<i>Scanning Electron Microscopy (SEM)</i>	83
2.7.3.	<i>Transmission Electron Microscopy (TEM)</i>	84
2.7.4.	<i>Energy Dispersive X- Ray Spectroscopy (EDS)</i>	85
2.7.5.	<i>X-Ray Diffraction (XRD)</i>	87
	References	88
CHAPTER 3		
	Experimental	102
3.1	Introduction	103
3.1.1.	Reagents and Materials.....	103
3.1.2.	Synthesis.....	104
3.1.2.1.	<i>Synthesis of Nanostructured Iron(II) and Cobalt(II)</i> <i>Phthalocyanines</i>	104

3.1.2.2.	<i>Synthesis of Iron(II) and Cobalt(II)</i>	
	<i>Octabutylsulphonylphthalocyanines</i>	105
3.1.2.3.	<i>Synthesis of Iron(II) tetrakis(diaquaplatinum) octa-</i>	
	<i>carboxyphthalocyanine (C₄₀H₂₄N₈FeO₂₄Pt₄)</i>	107
3.1.3.	<i>Purification of Multi-Walled Carbon Nanotubes</i>	109
3.1.4.	<i>Electrode Modification Procedure</i>	110
3.1.5.	<i>Electrochemical Procedure and Instrumentation</i>	111
	References	115

SECTION B

RESULTS AND DISCUSSION

CHAPTER 4

Microscopic, Spectroscopic, Electrochemical and Electrocatalytic Properties of Nanostructured Iron(II) and Cobalt(II)

Phthalocyanine..... 116

4.1 Microscopic and Spectroscopic Characterisation 117

4.1.1. *Comparative SEM, AFM and EDX*..... 117

4.2 Electrochemical Characterisation 120

4.2.1. *Electron transfer behaviour: cyclic voltammetry*..... 120

4.2.2. *Diffusion Domain Approximation Theory* 121

4.2.3.	<i>Electron transport behaviour: Impedimetric characterization</i>	124
.....		124
4.3	Electrocatalytic Properties	131
4.3.1.	<i>Electrocatalytic reduction of oxygen</i>	131
4.3.2.	<i>Electrocatalytic oxidation of thiocyanate</i>	140
4.3.3.	<i>Electrocatalytic oxidation of nitrite</i>	147
References		152
 CHAPTER 5		
Microscopic, Spectroscopic, Electrochemical and Electrocatalytic Properties of Iron(II) and Cobalt(II) Octabutylsulphonylphthalocyanine..... 156		
5.1	Microscopic and Spectroscopic Characterisation	157
5.1.1.	<i>SEM characterisation</i>	157
5.1.2.	<i>Characterization using UV-visible Spectrophotometer</i>	158
5.2	Electrochemical Characterisation	160
5.2.1.	<i>Solution Electrochemistry</i>	160
5.2.2.	<i>Electron transfer behaviour: cyclic voltammetry</i>	162
5.2.3.	<i>Electron transfer behaviour: impedimetric characterisation</i>	164
.....		164
5.3	Electrocatalytic Properties	168
5.3.1.	<i>Electrocatalytic reduction of oxygen</i>	168
5.3.1.1.	<i>Effect of scan rates</i>	170

5.3.1.2.	<i>Chronocoulometric studies</i>	172
5.3.1.3.	<i>Hydrodynamic voltammetry investigation</i>	173
5.3.2.	<i>Electrocatalytic oxidation of thiocyanate</i>	176
5.3.3.	Electrocatalytic oxidation of nitrite	177
References		179

CHAPTER 6

Microscopic, Spectroscopic, Electrochemical and Electrocatalytic Properties of Iron(II) tetrakis(diaquaplatinum)octa-carboxy

phthalocyanine..... 181

6.1. Microscopic and Spectroscopic Characterisation 182

Microscopic and spectroscopic information of iron..... 182

6.1.1. *UV-visible characterisation* 182

6.1.2. *Elemental analysis and mass spectroscopy characterisation*
..... 183

6.1.3. *XRD and EDX Characterisation*..... 184

6.1.4. *Comparative SEM and TEM characterisation* 185

6.2. Electrochemical Properties..... 187

6.2.1. *Solution electrochemistry*..... 187

6.2.2. *Electron transfer behaviour: cyclic voltammetry*..... 189

6.2.3.	<i>Electron transfer behaviour: Impedimetric characterisation</i>	191
.....		
6.3	Electrocatalytic Properties	195
6.3.1.	<i>Electrocatalytic reduction of oxygen</i>	195
6.3.2.	<i>Electrocatalytic oxidation of formic acid</i>	200
6.3.2.1.	<i>Comparative cyclic voltammetric response</i>	200
6.3.2.2.	<i>Chronoamperometry experiment</i>	204
6.3.2.3.	<i>Concentration studies: Tafel analysis</i>	206
6.3.2.4.	<i>Electrochemical impedance spectroscopy experiments</i>	209
6.3.2.5.	<i>Tolerance to carbon monoxide poisoning</i>	213
References		215
Conclusions and Future Perspectives		218
CONCLUSIONS		219
FUTURE PERSPECTIVES		221
APPENDIX A		222
List of scientific publications		222
APPENDIX B		224
List of scientific conferences		224

Abbreviations

A	Electrode surface area (cm ²)
AFM	Atomic force microscopy
Ag	Silver wire pseudo-reference electrode
Ag AgCl	Silver/silver chloride reference electrode
CME	Chemically modified electrode
C.E.	Counter electrode
CTAB	Hexadecyltrimethylammonium bromide
CV	Cyclic voltammetry
CV	Cyclic voltammogram
D	Diffusion coefficient (cm ² s ⁻¹)
DBU	1,8-diazacyclo[5.4.0]undec-7-ene
DMF	Dimethylformamide
EDX	Energy dispersive x-ray
EIS	Electrochemical impedance spectroscopy
EPPGE	Edge plane pyrolytic graphite electrode
FeOBSPc	Iron(II) octabutylsulphonylphthalocyanine
Fe(CN) ₆ ⁴⁻	Hexacyanoferrate(II)
Fe(CN) ₆ ³⁻	Hexacyanoferrate(III)
LoD	Limit of detection
MPc	Metallophthalocyanine
Pc	Phthalocyanine

PtFeOCPC	Iron(II) tetrakis(diaquaplatinum)octacarboxy phthalocyanine
R.E.	Reference electrode
SEM	Scanning electron microscope
SWV	Square wave voltammetry
T	Temperature (K)
t	Time(s)
TBAP	Tetrabutyl ammonium perchlorate
TEM	Transmission electron microscope
UV-vis.	Ultra violet visible spectrophotometer
W.E.	Working electrode
XRD	X-ray diffraction spectroscopy

List of Symbols

α	Transfer coefficient
ω	Angular velocity
Γ	Surface concentration
π	Pi bonding
λ	Wavelength
γ	kinematic viscosity
c	Molar concentration of analyte
C	Capacitance
C_{dl}	Double-layer capacitance
CPE	Constant phase element
D	Diffusion coefficient
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
E	Potential
E°	Standard potential
$E_{1/2}$	Half-wave potential
ΔE	Potential 'width'
ΔE_p	Anodic-to-cathodic peak potential separation
ΔE_s	Step height
ΔE_{sw}	Pulse height
f	Frequency
F	Faraday constant

H_z	Hertz
i_{pa}	Anodic peak current
i_{pc}	Cathodic peak current
j_{pa}	Anodic peak current density
j_{pc}	Cathodic peak current density
K	Kelvin
k_{app}	Apparent electron transfer rate constant
k_{cat}	Catalytic rate constant
n	Number of electron
Q	Electrical charge (C)
R	Universal gas constant
R_{ct}	Charge transfer resistance
R_s	Resistance of electrolyte
v	Scan rate
V	Volts
$-Z''$	Imaginary impedance
Z'	Real impedance
Z_w	Warburg impedance

List of Schemes

Scheme 2.1: <i>Schematic presentation of a catalytic process promoted by MPc electrode</i> ³³	34
Scheme 2.2: <i>General synthetic routes for Metallophthalocyanines</i>	63
Scheme 2.3: <i>Synthetic routes for peripherally and non-peripherally substituted MPc</i>	64
Scheme 2.4: <i>Synthetic route for octacarboxy-metallophthalocyanine</i> ⁹¹	65
Scheme 2.5: <i>Synthetic route for axial-ligated MPcs</i> ^{92,93}	65
Scheme 2.6: <i>Gouterman's four – orbital model</i> ⁹⁴	67
Scheme 2.7: <i>Energy level diagram of one-electron ring oxidised and one-electron ring reduced MPc complex</i> ⁹⁴	69
Scheme 2.8: <i>Possible adsorption mechanism of oxygen on a metal complex</i>	73
Scheme 2.9: <i>Series-parallel reaction scheme for oxygen reduction</i> ¹²⁵	75

List of Tables

Table 2.1: <i>The diagnostic criteria for reversible, irreversible and quasi-reversible cyclic voltammetric process</i>	24
Table 4.1: <i>Impedance parameters obtained for the various electrodes studied in 0.1 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$ 1.0 M KCl solution</i>	130
Table 5.1: <i>Redox potentials of compounds recorded in DMF containing 0.1 M TBAP.</i>	160
Table 5.2: <i>Impedance parameters obtained for the various electrodes studied in 0.1 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in 1 M KCl solution</i>	167
Table 6.1: <i>Redox potentials of FeOCPC and PtFeOCPC compounds recorded in DMF containing 0.1 M TBAP</i>	189
Table 6.2: <i>Impedance parameters obtained for the various electrodes studied in 0.1 M $[\text{Fe}(\text{CN})_6]^{3-/4-}$ 1.0 M KCl solution using the electrical equivalent circuit in Figure 6.7.</i>	194
Table 6.3: <i>Impedance data obtained for EPPGE-MWCNT-PtFeOCPC electrode studied in 0.5 M H_2SO_4 containing 0.5 M HCOOH at different potentials using the electrical equivalent circuit in Figure 6.14.</i>	212

List of Figures

Figure 2.1: <i>Model of the electrode-solution double layer</i>	13
Figure 2.2: <i>The potential-time waveform and a typical cyclic voltammogram for a reversible redox process⁷</i>	17
Figure 2.3: <i>Typical cyclic voltammogram for an irreversible redox process</i>	22
Figure 2.4: <i>Typical cyclic voltammogram for a quasi-reversible redox process</i>	23
Figure 2.5: <i>Symmetric “bell-shaped” cyclic voltammogram for surface confined redox system⁷</i>	24
Figure 2.6: <i>Square wave voltammetry potential-time waveform: sum of staircase and synchronized square wave</i>	27
Figure 2.7: <i>Typical square wave voltammetric response</i>	28
Figure 2.8: <i>Potential step chronoamperometry: (a) schematic application of potential step and (b) chronoamperometric response</i>	30
Figure 2.9: <i>Chronocoulometric response (a) chronocoulometric charge vs. square root of time plot (b). Dashed curves in (a) displayed for the illustration of the capacitive charge effect, the dashed, horizontal line represents the charge response in the absence of reactant</i>	31
Figure 2.10: <i>Sinusoidal voltage perturbation and current response (a), impedance presentation in the complex plane (b)</i>	36

Figure 2.11: Nyquist (a) and Bode (b) plots for presentation of impedance data	37
Figure 2.12: Classical Randles electrical equivalent circuit for an ideal behaviour	38
Figure 2.13: Modified Randles equivalent circuit showing the CPE for non-ideal behaviour	40
Figure 2.14: The structure of graphite electrode ⁷	48
Figure 2.15: Interwoven ribbons of graphite structure	49
Figure 2.16: Schematic representation of a step edge on a HOPG surface ⁴⁸	51
Figure 2.17: Geometric structures of (a) SWCNT and (b) MWCNT ...	57
Figure 2.18: Unit cells of carbon nanotubes	57
Figure 2.19: The types of carbon nanotubes created from how the graphene sheet is rolled	58
Figure 2.20: Geometric structure of metallophthalocyanine.....	62
Figure 2.21: Typical electronic absorption spectra of phthalocyanine showing the B and Q bands (A) and the charge transfer transition (B).....	66
Figure 2.22: AFM 3-D topographical image of iron(II) pthalocyanine on glassy carbon plate	82
Figure 2.23: High resolution SEM image of multi-walled carbon nanotubes.....	84
Figure 2.24: TEM image of multi-walled carbon nanotubes.....	85

Figure 3.1: Diagrammatic presentation of a conventional three-electrode system..... 112

Figure 4.1: AFM images of bulk FePc (A) and nanostructured FePc (B) 118

Figure 4.2: EDX profile of bulk FePc (A), CTAB (B) and nanoFePc (C) 119

Figure 4.3: Comparative cyclic voltammograms of the electrodes in 1.0 M KCl containing 0.1 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ solution (a) FePc derivatives (b) CoPc derivatives 122

Figure 4.4: Comparative (FePc derivatives) Nyquist plots (a) and Bode plots (b) and (c) obtained for the various electrodes studied in 1.0 M KCl containing 0.1 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$, equivalent electrical circuit diagrams (d) 128

Figure 4.5: Comparative (CoPc derivatives) Nyquist plots (a) and Bode plots (b) and (c) obtained for the various electrodes studied in 1 M KCl containing 0.1 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$, equivalent electrical circuit diagrams (d) 129

Figure 4.6: Comparative cyclic voltammograms of the various electrodes in oxygen saturated 0.1 M NaOH solution. FePc derivatives (a), CoPc derivatives (b) 133

Figure 4.7: Comparative cyclic voltammograms of the different electrodes in nitrogen saturated 0.1 M NaOH (a) EPPGE-MWCNT, (b) EPPGE-MWCNT-nanoFePc. Scan rate: 25 mV s^{-1} 134

- Figure 4.8:** *RDE polarization curves of EPPGE-MWCNT-nanoFePc in oxygen saturated 0.1 M NaOH solution..... 135*
- Figure 4.9:** *Koutecky-Levich plot (a) and Tafel plot (b) of EPPGE-MWCNT-nanoFePc generated from Figure 4.8..... 137*
- Figure 4.10:** *Comparative cyclic voltammograms of the various electrodes in 1 mM SCN⁻ solution contained in phosphate buffer (pH 5). FePc derivatives (a), CoPc derivatives (b) 141*
- Figure 4.11:** *Cyclic voltammetric evolutions at different scan rates of (a) EPPGE-MWCNT-nanoFePc and (b) of EPPGE-MWCNT-nanoCoPc in 1.0 mM of thiocyanate (pH 5). Plots of peak current density vs. square root of scan rate (c) EPPGE-MWCNT-nanoFePc and (d) of EPPGE-MWCNT-nanoCoPc 142*
- Figure 4.12:** *Current function plots: (a) EPPGE-MWCNT-nanoFePc, (b) EPPGE-MWCNT-nanoCoPc and Tafel plots: (c) EPPGE-MWCNT-nanoFePc, (d) EPPGE-MWCNT-nanoCoPc 144*
- Figure 4.13:** *Chronoamperometric evolutions obtained at the EPPGE-MWCNT-nanoFePc (a) and EPPGE-MWCNT-nanoCoPc (b) electrodes in the absence and presence of consecutive addition of 40 μM thiocyanate in phosphate buffer solution (pH 5). Insets, plot of peak current density vs. concentration of thiocyanate..... 146*

- Figure 4.14:** *Comparative cyclic voltammograms of the various electrodes in 1mM nitrite solution contained in phosphate buffer (pH 7.4). FePc derivatives (a), CoPc derivatives (b) 147*
- Figure 4.15:** *Cyclic voltammetric evolutions at different scan rates of (a) EPPGE-MWCNT-nanoFePc and (b) of EPPGE-MWCNT-nanoCoPc in 1.0 mM of nitrite (pH 7.4). Plots of peak current density vs. square root of scan rate (c) EPPGE-MWCNT-nanoFePc and (d) of EPPGE-MWCNT-nanoCoPc 148*
- Figure 4.16:** *Current function plot (a) EPPGE-MWCNT-nanoFePc, (b) EPPGE-MWCNT-nanoCoPc and Tafel plot (c) EPPGE-MWCNT-nanoFePc, (d) EPPGE-MWCNT-nanoCoPc.... 149*
- Figure 4.17:** *Chronoamperometric evolutions obtained at the EPPGE-MWCNT-nanoFePc (a) and EPPGE-MWCNT-nanoCoPc (b) electrodes in the absence and presence of consecutive addition of 40 μ M nitrite in phosphate buffer solution (pH 7.4).Insets, plot of peak current density vs. concentration of nitrite 151*
- Figure 5.1:** *SEM images of MOBSPc (a), MWCNT (b) and MWCNT/MOBSPc..... 157*
- Figure 5.2:** *UV-visible spectrum of CoOBSPc (bold lines) and FeOBSPc (dashed lines) in chloroform. 158*

- Figure 5.3:** *Typical cyclic voltammograms and inset square wave voltammograms for FeOBSPc (a) and CoOBSPc (b) recorded in DMF containing 0.1 M TBAP. 161*
- Figure 5.4:** *Comparative cyclic voltammograms of the various electrodes in 0.1 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in 1.0 M KCl solution. 163*
- Figure 5.5:** *(a) Comparative Nyquist and (b), (c) Bode plots of the various electrodes in 0.1 M $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ 1.0 M KCl solution. Proposed equivalent electrical circuits (d) 166*
- Figure 5.6:** *Comparative cyclic voltammograms of the electrodes in 0.1 M NaOH saturated with oxygen. Scan rate: 10 mV s^{-1} 169*
- Figure 5.7:** *(a) Cyclic voltammetric evolutions of the EPPGE-MWCNT-FeOBSPc electrode at varying scan rates. Inset shows linear relationship between the reduction peak current (I_p) and square root of scan rate ($v^{1/2}$). (b) Plot of peak potential (E_p) against the logarithm of scan rate ($\log v$). 171*
- Figure 5.8:** *(a) Chronocoulometry curves of EPPGE-MWCNT-FeOBSPc in 0.1 M NaOH saturated with oxygen (bold line) and saturated with nitrogen (dashed line). (b) Plot of charge (Q) against square root of time ($t^{1/2}$). 173*

- Figure 5.9:** (a) RDE voltammetry for oxygen reduction on an EPPGE-MWCNT- FeOBSPc electrode in oxygen saturated 0.1 M NaOH. Scan rate: 10 mV s⁻¹. (b) Koutecky-Levich plots for oxygen reduction on EPPGE-MWCNT-FeOBSPc electrode in oxygen saturated 0.1 M NaOH solution. . 175
- Figure 5.10:** Comparative cyclic voltammograms of the various electrodes in 1mM thiocyanate solution contained in phosphate buffer (pH 5). 177
- Figure 5.11:** Comparative cyclic voltammograms of the various electrodes in 1mM nitrite solution contained in phosphate buffer (pH 7.4)..... 178
- Figure 6.1:** Comparative UV-visible spectrum of FeOCPC and PtFeOCPC in DMF 182
- Figure 6.2:** High resolution mass spectra of iron(II) tetrakis (diaquaplatinum)octa-carboxyphthalocyanine (C₄₀H₂₄N₈FeO₂₄Pt₄)..... 183
- Figure 6.3:** Comparative XRD pattern of FeOCPC and PtFeOCPC (a), EDX spectra of PtFeOCPC (b)..... 185
- Figure 6.4:** Typical SEM images of MWCNT-COOH (a) and MWCNT-COOH/PtFeOCPC (b). Typical TEM images of PtFeOCPC (c) and MWCNT-COOH/PtFeOCPC (d)..... 186
- Figure 6.5:** Typical cyclic voltammograms for FeOCPC (a) and PtFeOCPC (b) recorded in DMF containing 0.1 M TBAP. Insets, corresponding square wave voltammograms 187

Figure 6.6: *Comparative cyclic voltammograms of the various electrodes in 0.1 M [Fe(CN)₆]^{3-/4-} 1.0 M KCl solution. 190*

Figure 6.7: *Comparative Nyquist plots (a) and Bode plots: (b) and (c) of the various electrodes in 0.1 M [Fe(CN)₆]^{3-/4-} 1.0 M KCl solution. Equivalent electrical circuit used for fitting the measured data (d). 193*

Figure 6.8: *Comparative linear sweep voltammetric curves of the electrodes in oxygen saturated 0.1 M NaOH solution. Scan rate: 10 mV s⁻¹ 195*

Figure 6.9: *(a) RDE polarization curves at different rotation rates for EPPGE-MWCNT-PtFeOCpC electrode in oxygen saturated 0.1 M NaOH solution scan rate 10 mVs⁻¹; (b) Koutecky-Levich plot obtained from RDE data 198*

Figure 6.10: *Tafel plot of E_{app} vs. log j_K for oxygen reduction on EPPGE-MWCNT-PtFeOCpC electrode in oxygen saturated 0.1 M NaOH solution..... 200*

Figure 6.11: *Cyclic voltammograms of the various electrodes in 0.5 M H₂SO₄ containing 0.5 M HCOOH solutions 203*

Figure 6.12: *Chronoamperometric curves of EPPGE-PtFeOCpC and EPPGE-MWCNT-PtFeOCpC in 0.5 M H₂SO₄ containing 0.5 M HCOOH solutions 206*

- Figure 6.13:** *Cyclic voltammetric evolutions following changes in concentration of formic acid (a), Tafel plots of η against $\log j$ at different concentration of formic acid (b)..... 208*
- Figure 6.14:** *Typical Nyquist(a), Bode (b and c) plots and equivalent circuit (d) used to fit the spectra obtained at different potentials (0.10, 0.35, 0.55, 0.75 and 0.95 V) for EPPGE-MWCNT-PtFeOCpC in 0.5 M H₂SO₄ containing 0.5 M HCOOH..... 211*
- Figure 6.15:** *Comparative cyclic voltammograms of EPPGE-PtFeOCpC (a) and EPPGE-MWCNT-PtFeOCpC (b) electrodes studied in 0.5 M H₂SO₄ (I), CO saturated in 0.5 M H₂SO₄ (II) and CO saturated in 0.5 M H₂SO₄ and 0.5 M HCOOH (III) 214*