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Electrochemical and Electrocatalytic Properties of Carbon Nanotubes Integrated with Selected Metal and Metal Oxide Nanoparticles

by

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DECLARATION

I declare that the dissertation which is hereby submitted to the Department of Chemistry, Faculty of Natural and Agricultural Sciences, University of Pretoria, is my work and has not been submitted by me for a degree at any other University, and that all material contained therein has been duly acknowledged.

DEDICATION

This dissertation is dedicated first to the glory of the Almighty Allah for giving me the strength to see the end of the programme despite all odds. And my parents, Engineer Alabi Saubana Adekunle, Mr Tajudeen Ayinla Adekunle and Mrs Agbeke Temilola Adekunle for their unquantified support.

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ABSTRACT

This work describes metal (M) and metal oxides (MO) films (where M = Ni, Co and Fe) obtained by electrosynthesis and chemical synthesis, and modified with carbon nanotubes (CNTs) on edged plane pyrolytic graphite electrode (EPPGE). The MO nanoparticles investigated are nickel oxide (NiO), cobalt oxide (Co_3O_4) and iron oxide (Fe_2O_3). Successful modification of the electrodes with the M or MO/CNT nanocomposite was confirmed by field emission scanning electron microscopy (FESEM), high resolution scanning electron microscopy (HRSEM), high resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM), x-ray diffraction spectroscopy (XRD), x-ray photoelectron spectroscopy (XPS), electron dispersive x-ray spectroscopy (EDX), fourier transformed infra-red spectroscopy (FTIR) and ultraviolet-visible (UV-vis) spectroscopy. Electron transport (ET) properties of the modified electrodes was explored using cyclic voltammetry (CV) and electrochemical impedance spectroscopic techniques (EIS) with ferricyanide/ferrocyanide ($[Fe(CN)_6]^{3-/4-}$) as the redox probe. The electron transfer constant (k^0) differs in terms of materials, method of synthesis and electrical equivalent circuits used in the fitting or modelling process. Generally, the k^0 values are in the 10^{-3} – 10^{-2} cms^{-1} with Ni nanoparticles having the highest k^0 or fastest electron transport. The presence of CNTs also enhances the ET compared

with electrodes without CNTs. The electrocatalytic properties of the modified electrodes were explored using the following analytical probes: diethylaminoethanethiol (DEAET), hydrazine, nitrite and dopamine. The study showed that the electrocatalytic oxidation of DEAET and hydrazine was favoured on electrode modified with Ni nanoparticles; nitrite and dopamine were best catalysed by the Co and Fe_2O_3 nanoparticles, respectively. Electroanalysis results (using chronoamperometry, square wave voltammetry and linear sweep voltammetry) indicated some level of adsorption of DEAET, hydrazine and nitrite on the modified electrode, while dopamine electrocatalytic oxidation and detection followed a simple diffusion-controlled process. The adsorption process was found to be physically induced and could be eliminated by repetitive cycling of the electrode in the aqueous electrolyte solution. Electrodes modified with chemically-synthesised material (particularly nickel) were less adsorptive towards DEAET and hydrazine detection, and gave sensitivity and limit of detection values that compared with data obtained using electrochemical deposition / synthesis. The chemical stability and reproducibility of the modified electrodes were determined and discussed. Finally, electrochemical properties were studied to help screen these electrode materials in supercapacitors. CNT-NiO nanocomposites exhibit remarkable supercapacitive behaviour in neutral and acidic media compared to the other CNT-MO nanocomposites investigated. Interestingly, the

capacitive behaviour of the CNT-NiO was more enhanced in H_2SO_4 solution than in Na_2SO_4, possibly due to the high conductivity of the former. The CNT-NiO electrode maintained good stability with only about 5% loss of its specific capacitance after 1000 cycle life.

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LIST OF ABBREVIATIONS

A	Electrode surface area (cm^{-2})
AFM	Atomic force microscopy
Ag	Silver wire pseudo-reference electrode
Ag/AgCl	Silver/silver chloride reference electrode
BPPGE	Basal plane pyrolytic graphite electrode
CA	Chronoamperometric
CME	Chemically modified electrode
CNT	Carbon nanotubes
CV	Cyclic voltammetry
CV	Cyclic voltammogram
DMF	Dimethylformamide
EIS	Electrochemical impedance spectroscopy
EPPGE	Edge plane pyrolytic graphite electrode
EPPGE-SWCNT	Edge plane pyrolytic graphite electrode decorated single-walled carbon nanotubes
$Fe_4(III)[Fe(II)(CN)_6]^3$	Divalent iron (II)/(III) cyanide complex
FTIR	Fourier transform infrared
GCE	Glassy carbon electrode
LCR	Linear concentration range
LoD	Limit of detection
LSV	Linear sweep voltammetry
MMPs	Magnetic nanoparticles
MWCNT	Multi-walled carbon nanotubes
NPs	Nanoparticles
OSWV	Osteryoung square wave voltammogram
PBS	Phosphate buffer solution
R.E.	Reference electrode
R_{ad}	Resistance due to adsorption
SAM	Self-assembled monolayer
SCE	Standard calomel electrode

SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotubes.
SWCNT-PABS	Poly(m-aminobenzenesulphonated) single-walled carbon nanotubes
SWV	Square wave voltammetry
W.E.	Working electrode
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

A	Rate of electron transfer
Γ	Surface coverage or concentration
π	Pi bonding
λ	Wavelength
A	Absorbance
C	Molar concentration of analyte
C	Capacitance
C_{dl}	Double-layer capacitance
CPE	Constant phase electrode
C_{Ox}	Concentration of the oxidized form of an analyte
C_{Red}	Concentration of the reduced form of an analyte
C_s	Specific interfacial capacitance
d	Diameter
D	Diffusion coefficient
E_f	Final potential
E_i	Starting potential
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
E	Potential
E^o	Standard potential
$E_{1/2}$	Half-wave potential
ΔE_p	Anodic-to-cathodic peak potential separation
f	Frequency
F	Faraday constant

h	Plank's constant
Hz	Hertz
I_{abs}	Absorbed light
i_{pa}	Anodic peak current
i_{pc}	Cathodic peak current
k	Heterogeneous electron transfer coefficient
K	Equilibrium constant
K_a	Dissociation constant
K	Kelvin
N	Number of electron
N_A	Avogadro's constant
q	Electrical charge
Q	Electrical charge (C)
R	Universal gas constant
R_{ct}	Charge transfer resistance
R_s	Resistance of electrolyte
ν	Scan rate
V	Volts
Z_{im}	Imaginary impedance
Z_{re}	Real impedance
Z_w	Warburg impedance

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