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Electrochemical and electrocatalytic properties of self-assembled single-walled carbon nanotube/organo-iron hybrid systems on gold electrodes

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by

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DEDICATION

This dissertation is dedicated to my promoter, Dr K. I. Ozoemena, for

everything he has done.

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.

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ABSTRACT

This work describes, for the first time, the electrochemical and electrocatalytic properties of self-assembled layers of single-walled carbon nanotubes (SWCNTs) intergrated with selected organo-iron complexes and Cysteamine (Cys) forming a base on gold electrodes. The organo-iron complexes selected for this study were octa(hydroxyethylthio)phthalocyaninatoiron(II) (FeOHETPc), tetraaminophthalocyninatoiron(II) (FeTAPc), tetraaminophthalocyninatocobalt(II) (CoTAPc), ferrocene monocarboxylic acid (FMCA), ferrocene dicarboxylic acid (FDCA) or a mixture of SWCNT and FMCA or FDCA. The successful fabrication of these electrodes were established using atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and electrochemical techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), square wave voltammetry (SWV) and chronoamperometry (CA)

The Au-Cys-SWCNT-FeOHETPc electrode exhibited strong dependence on the reaction of the head groups and the pH of the working electrolytes. The high electron transfer capability of the Au-Cys-SWCNT-FeOHETPc electrode over other electrodes as the Au-Cys-SWCNT or the Au-Cys-FeOHETPc or the Au-FeOHETPc suggests that

SWCNT greatly improves the electronic communication between FeOHETPc and the bare gold electrode. The electron transfer rate constant (k_{app}) of Au-Cys-SWCNT-FeOHETPc in pH 4.8 conditions (~1.7 x 10^{-2} cm s^{-1}) over that of the electrode obtained from SWCNT integrated with tetraaminophthalocyninatocobalt(II) (Au-Cys-SWCNT-CoTAPc) (5.1 x 10^{-3} cm s^{-1}) is attributed to the possible effect of both the central metal on the phthalocyanine core and subsituents on the peripheral positions of the phthalocyanine rings.

This work clearly proved that the aligned SWCNTs arrays exhibit much faster electron transfer kinetics to redox-active species in solutions compared to the randomly dispersed (drop-dried) SWCNTs. The advantageous electron transfer properties of the aligned Au-Cys-SWCNT-FeOHETPc electrode, coupled with its ease of fabrication and electrochemical stability, could be found useful in electrochemical sensing and catalysis.

Thiocyanate ion was used as an analytical probe to examine the electrocatalytic properties of these modified gold electrodes. This work shows that SWCNT-FeOHETPc hybrid exhibits excellent sensitivity towards the detection of thiocyanate compared to electrodes containing SWCNT or FeTAPc or FeOHETPc only, indicating the ability of the SWCNTs to function as effective conductive nanowires for the detection of this important analyte. The electrochemical response of

the FeOHETPc based electrodes was greater than their FeTAPc-based electrode counterparts, indicative of the impact of peripheral substituents on the phthalocyanine core towards electrocatalytic behaviour of these types of hybrids. Nevertheless, the exchange of the central metal as seen with the case of CoTAPc (see chapter 3), provide useful comparative electrochemical activity of this complexes versus FeTAPc with the same chemical environment with an indication of iron being the best as metal centre.

FMCA or FDCA were covalently attached to the base Cysteamine monolayer to form the Au-Cys-FMCA and Au-Cys-FDCA, respectively. The same covalent attachment strategy was used to form the mixed SWCNTs and ferrocene-terminated layers (i.e., Au-Cys-SWCNT/FMCA and Au-Cys-SWCNT/FDCA). The impact of neighbouring SWCNTs on the electron transfer dynamics of the ferrocene molecular assemblies in acidic medium (0.5 M H_2SO_4) and in a solution (pH 7.2) of an outer-sphere redox probe ($[Fe(CN)_6]^{4-}$/ $[Fe(CN)_6]^{3-}$) was explored. The electron transfer rate constants in both solution media essentially decrease as Au-Cys-FMCA > Au-Cys-SWCNT/FDCA > Au-Cys-FDCA > Au-Cys-SWCNT/FMCA. This trend has been interpreted in terms of several factors such as the locations of the ferrocene species in a range of environments with a range of potentials, the proximity /interactions of the ferrocenes with one another, and electrostatic

interaction or repulsion existing between the negatively-charged redox probe and the modified electrodes.

Square wave voltammetry was used to examine the catalytic behaviour of the electrodes. Au-Cys-SWCNT/FDCA proved to be the best electrode, possibly due to the repulsive interactions between the negatively charged SCN^- and high number of surface –COOH species at the SWCNT/FDCA. This novel study has provided some useful insights as to how CNTs co-assembled with ferrocene-terminated thiols could impact on the heterogeneous electron transfer kinetics as well as the electrocatalytic detection of the self-assembled ferrocene layers.

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ABBREVIATIONS

A	Electrode surface area (cm^2)
AFM	Atomic force microscopy
Ag	Silver wire pseudo-reference electrode
AglAgCl	Silver/silver chloride reference electrode
CME	Chemically modified electrode
C.E.	Counter electrode
CMEs	Chemically modified electrodes
CV	Cyclic voltammetry
Cys	Cysteamine
CV	Cyclic voltammogram
D	Diffusion coefficient (cm^2s^{-1})
DCC	Dicyclohexylcarbodiimide
DMF	Dimethylformamide
EIS	Electrochemical impedance spectroscopy
E_p	Peak potential
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
E^o	Standard potential
$E^{o'}$ or $E_{1/2}$	Formal redox potential
F	Faraday's constant
FeOHETPc	Iron-octahydroxyethylthiophthalocyanine

$Fe(CN)_6^{4-}$	Hexacyanoferrate(II)
$Fe(CN)_6^{3-}$	Hexacyanoferrate(III)
i_{for}	Forward current
i_{rev}	Reverse current
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
ITO	Indium tin oxide
LoD	Limit of detection
MPc	Metallophthalocyanine
MPc-SAM	Metallophthalocyanine-self assembled monolayer
Pc	Phthalocyanine
R	Gas constant
R.E.	Reference electrode
R_s	Solution resistance
SAM	Self-assembled monolayer
SEM	Scanning electron microscopy
SWCNTs	Single-walled carbon nanotubes
SWV	Square wave voltammetry
T	Temperature (K)
t	Time(s)
W.E.	Working electrode
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

α	Transfer coefficient
ω	Angular velocity
ε	Extinction coefficient
Γ	Surface coverage or concentration
π	Pi bonding
λ	Wavelength
γ	kinematic viscosity
C	Molar concentration of analyte
c	Speed of light
C	Capacitance
C_{dl}	Double-layer capacitance
CPE	Constant phase electrode
C_m	Monolayer capacitance
C_{ox}	Concentration of the oxidised form of an analyte
C_{red}	Concentration of the reduced form of an analyte
D	Diameter
D	Diffusion coefficient
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's constant
h	Plank's constant
Hz	Hertz
i_{pa}	Anodic peak current
i_{pc}	Cathodic peak current
k	Heterogeneous electron transfer coefficient
k_{et}	Electron transfter rate constant
k_f	Rate of forward reaction
k_r	Rate of reverse/backward reaction
k_{obs}	Observed rate constant
K	Kelvin
K	Equilibrium constant
K_a	Dissociation constant
K_{aap}	Electron transfer rate constant
n	Number of electron
N_A	Avogadro's constant
q	Electrical charge
Q	Electrical charge (C)
r	Radius of electrode

R	Universal gas constant
R_{ct}	Charge transfer resistance
R_s	Resistance of electrolyte
Sub	Substrate
$Sub_{(ox)}$	Oxidised substrate
v	Scan rate
V	Volts
Z_{im}	Imaginary impedance
Z_{re}	Real impedance
Z_w	Warburg impedance

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