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Electrochemical properties of self-assembled films of single-walled carbon nanotubes, monolayer-protected clusters of gold nanoparticles and iron (II) phthalocyanines at gold electrodes

by

Jeseelan Pillay

Dissertation submitted in fulfilment of the requirements for the degree

of

Doctor of Philosophy

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Chemistry Department

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Supervisor: Dr. K. I. Ozoemena

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DECLARATION

I declare that the dissertation, which I hereby submit for the degree of Doctor of Philosophy in the Faculty of Natural and Agricultural Sciences at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

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JESEELAN PILLAY

s26518504

DEDICATION

To my dear friend and mentor Dr. Kenneth Ozoemena

"thank you for believing in me from Hons to PhD"

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my inspirational supervisor Dr. Kenneth Ozoemena for his uncompromising guidance that has helped me to improve in all aspects of my life. For his encouragement when I failed to get any results for almost a year, for his compassion whenever I had difficulties in my personal life but most of all for his confidence in me. It has been an honour and privilege to work alongside the best electrochemist in South Africa who has inspired me to continue research in this field.

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ABSTRACT

Electrochemical properties of self-assembled films of single-walled carbon nanotubes, monolayer-protected clusters of gold nanoparticles and iron (II) phthalocyanines at gold electrodes

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Supervisor: Dr. K. I. Ozoemena

Submitted in fulfilment of the requirements for the degree Doctor of Philosophy, University of Pretoria, Department of Chemistry

This dissertation investigates the heterogeneous electron transfer dynamics and electrocatalytic behaviour of the following molecules immobilized on gold electrode: **(a)** 2-dimethylaminoethanethiol (DMAET), with and without integration with *poly*(*m*-aminobenzenesulfonic acid) functionalised single-walled carbon nanotubes (SWCNT-PABS); **(b)** SWCNT-PABS and iron (II) phthalocyanine nanoparticles (*nano*FePc); **(c)** Colloidal gold / Gold nanoparticles (AuNP) and *nano*FePc **(d)**; water-soluble iron (II) tetrasulfophtalocyanine (FeTSPc) and SWCNT-PABS, and **(e)** novel monolayer protected gold nanoparticles (MPCAuNPs) by means of either (i) layer-by-layer (LBL) self-assembly or (ii) self-assembled monolayer (SAM) fabrication strategy.

Atomic force microscopy and electrochemical studies (cyclic voltammetry, and electrochemical impedance spectroscopic) were used to monitor the substrate build-up, via strong electrostatic interaction. The surface pK_a of DMAET was estimated at 7.6, smaller than its solution pK_a of 10.8. It is also shown that SWCNT-PABS is irreversibly attached to the DMAET SAM. For layered films involving SWCNT-PABS and *nano*FePc (Au-DMAET- SWCNT-PABS-*nano*FePc)$_n$ (n=1-5 layers) as the number of bilayers increase, the electron transfer kinetics of the $[Fe(CN)_6]^{3-/4}$ redox probe decreases. On the contrary, LBL assembly involving AuNP and *nano*FePc (Au-DMAET-AuNP-*nano*FePc)$_n$ (n=1-4 layers) shows an increase followed by a decrease in electron transfer kinetics subsequent to the adsorption of *nano*FePc and AuNP layers, respectively. For SAMs involving FeTSPc and SWCNT-PABS, the mixed hybrid (Au-DMAET-SWCNT-PABS/FeTSPc) exhibited fastest charge transport compared to other electrodes. For the novel MPCAuNPs, the protecting or stabilizing ligands investigated were the (1-sulfanylundec-11-yl) tetraethylene glycol (PEG-OH) and the (1-sulfanylundec-11-yl) polyethylene glycolic acid (PEG-COOH). Three different mass percent ratios (PEG-COOH : PEG-OH), viz. 1:99 (MPCAuNP-COOH$_{1\%}$), 50:50 (MPCAuNP-COOH$_{50\%}$) and 99:1 (MPCAuNP-COOH$_{99\%}$) were used to protect the gold nanoparticles. The impact of these different ratios on the electron transfer dynamics in

organic and aqueous media was explored. The average electron transfer rate constants (k_{et} / s^{-1}) in organic medium decreased as the concentration of the surface-exposed –COOH group in the protecting monolayer ligand increased: MPCAuNP-$COOH_{1\%}$ (~ 10 s^{-1}) > MPCAuNP-$COOH_{50\%}$ (~ 9 s^{-1}) > MPCAuNP-$COOH_{99\%}$ (~ 1 s^{-1}). In aqueous medium, the trend is reversed. This behaviour has been interpreted in terms of the hydrophobicity (quasi-solid nature) and hydrophilicity (quasi-liquid nature) of the terminal –OH and –COOH head groups, respectively. The ionization constants of the terminal groups (i.e., surface pK_a) was estimated as ~ 8.2 for the MPCAuNP-$COOH_{1\%}$, while both MPCAuNP-$COOH_{50\%}$ and MPCAuNP-$COOH_{99\%}$ showed two pK_a values of about 5.0 and ~ 8.0, further confirming the hydrophilicity / hydrophobicity of these surface functional groups.

Hydrogen peroxide (H_2O_2), epinephrine (EP) and ascorbic acid (AA) were used as model analytes to examine electrocatalytic ability of these nanostructured assemblies. The electrochemical reduction of H_2O_2 at a constant concentration was amplified upon increasing bilayer formation of SWCNT-PABS and *nano*FePc, while SWCNT-PABS/FeTSPc showed the best response towards the detection of epinephrine. MPCAuNP-$COOH_{99\%}$ showed an excellent suppression of the voltammetric response of the AA and an enhanced electrocatalytic activity towards the detection of EP compared to the other MPCAuNPs.

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LIST OF ABBREVIATIONS

AA	=	Ascorbic acid
AFM	=	Atomic Force Microscopy
Ag|AgCl	=	Silver|silver Chloride Reference Electrode
CA	=	Chronoamperometry
CE	=	Counter Electrode
CME	=	Chemically Modified Electrode
CNT	=	Carbon Nanotube
CPE	=	Constant Phase Angle Element
CV	=	Cyclic Voltammetry / Cyclic Voltammetric
CVD	=	Chemical Vapour Decomposition
DMAET	=	Dimethylaminoethanethiol
DMF	=	*N*,*N*-Dimethylformamide
EDX	=	Energy-Dispersive X-Ray
EIS	=	Electrochemical Impedance Spectroscopy
EP	=	Epinephrine
FeTSPc	=	Iron (II) Tetrasulphonated Phthalocyanine
GCE	=	Glassy Carbon Electrode
H_2O_2	=	Hydrogen peroxide
IHP	=	Inner Helmholtz Plane
IR	=	Infra-Red
IUPAC	=	International Union of Pure and Applied

$K_3Fe(CN)_6$	=	Potassium hexacyanoferrate(III)
$K_4Fe(CN)_6$	=	Potassium hexacyanoferrate(II)
KCl	=	Potassium Chloride
LBL	=	Layer-by-layer
LoD	=	Limit of Detection
LSV	=	Linear Sweep Voltammetry
MES	=	Sodium 2-Mercaptoethanesulphonate
MPc	=	Metallophthalocyanine
MPCAuNPs	=	Monolayer-Protected Clusters of Gold
MPCs	=	Monolayer-protected Clusters
MTAPc	=	Metallotetraamino-phthalocyanine
MWCNT	=	Multi-Walled Carbon Nanotube
NaCl	=	Sodium Chloride
*nano*FePc	=	nano Iron (II) Phthalocyanine nanoparticles
OHP	=	Outer Helmholtz Planes
PBS	=	Phosphate Buffer Solutions
Pc	=	Phthalocyanine
PEG	=	Polyethylene Glycol
R_{ct}	=	Charge Transfer Resistance
RDE	=	Rotating Disc Electrode
RE	=	Reference Electrode

R_s	=	Solution Resistance
SAM	=	Self-Assembled Monolayer
SEM	=	Scanning Electron Microscopy
SWCNT	=	Single-Walled Carbon Nanotube
SWCNT-PABS	=	Single-Walled Carbon Nanotubes poly (*m*- aminobenzene sulfonic acid)
SWV	=	Square Wave Voltammetry
$TBABF_4$	=	Tetrabutylammonium Tetrafluoroborate
TEM	=	Transmission Electron Microscopy
UV-vis	=	Ultraviolet-visible
WE	=	Working Electrode
Z_w	=	Warburg Impedance

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