

Nanocomposites of Carbon Nanomaterials and Metallophthalocyanines: Applications Towards Electrocatalysis.

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DEDICATION

To

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(Mwanasikana wababa/Dad's daughter)

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Abstract

Nanohybrid materials have been prepared and examined for their electrocatalytic activity. The nanocomposites have been prepared from carbon nanomaterials (multiwalled carbon nanotubes (MWCNTs) and graphene nanosheets), cadmium selenide quantum dots and metallophthalocyanines (MPcs). The MPcs used in this work are cobalt tetraamino-phthalocyanine (CoTAPc) and tetra (4-(4,6-diaminopyrimidin-2-ylthio) phthalocyaninatocobalt (II)) (CoPyPc). Their activity has also been explored in different forms; polymeric MPcs, iodine doped MPcs and covalently linked MPcs. The premixed drop-dry, sequential drop-dry and electropolymerisation electrode modification techniques were used to prepare nanocomposite catalysts on the glassy carbon electrode (GCE) surface. The sequential drop dry technique for MPc and MWCNTs gave better catalytic responses in terms of limit of detection, catalytic and electron transfer rate constants relative to the premixed. MWCNTs and CdSe-QDs have been used as intercalating agents to reduce restacking of graphene nanosheets during nanocomposite preparation. Voltammetry, chronoamperometry, scanning electrochemical microscopy and electrochemical impedance spectroscopy methods are used for electrochemical characterization modified GCE. X-ray photoelectron spectroscopy, X-ray diffractometry, transmission electron microscopy, scanning electron microscopy, infra-red spectroscopy, Raman spectroscopy were used to explore surface functionalities, morphology and topography of the nanocomposites. Electrocatalytic activity and possible applications of the modified electrodes were tested using oxygen reduction reaction, l-cysteine oxidation and paraquat reduction. Activity of

nanocomposites was found superior over individual nanomaterials in these applications.

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List of Abbreviations

BCNT = Boron-doped carbon nanotube.

BE = Binding energy.

CA = Chronoamperometry.

CCE = Carbon ceramic electrode.

CNTs = Carbon nanotubes.

CV = Cyclic voltammetry.

DBU = Dicyclohexylcarbodiimide.

DCC = Dicyclohexylcarbodiimide.

DMF = Dimethylformide.

DMSO = Dimethylsulfoxide.

EIS = Electrochemical Impedance Spectroscopy.

EPR = Electron paramagnetic resonance.

FRA = Frequency response analyser.

FTIR = Fourier transform infra-red.

FWHM = Full width at half maxima.

GCE = Glassy carbon electrode.

GONS = Graphene oxide nanosheets

GPES = General purpose electrochemical system.

HOMO = Highest occupied molecular orbital.

IMAC = Interim Maximum Acceptable Concentration.

LMCT = Ligand-to-metal charge transfer.

LOD = Limit of detection.

LUMO = Lowest unoccupied molecular orbital.

MLCT = Metal-to-Ligand charge transfer.

MS = Mass spectrometry.

MWCNTs = Multiwalled carbon nanotubes.

NLLS = Nonlinear least squares.

NPs = Nanoparticles.

OHETPc = octa(hydroxyethylthio)-phthalocyanine.

ORR = Oxygen reduction reaction.

Pc = Phthalocyanine.

PLOQ = Practical limit of quantification.

Poly-MPc = Polymerised metallophthalocyanine.

PQ = Paraquat.

PyPc = 4-(4,6-diaminopyrimidin-2-ylthio) phthalocyanine.

QDs = Quantum dots.

RDE = Rotating disk electrode.

rGNS = Reduced graphene nanosheets.

RSF = Relative sensitivity factor.

SAM= Self-assembled monolayer.

SECM = Scanning electrochemical microscopy.

SEM = Scanning electron microscopy.

SWCNTs = Single walled carbon nanotubes.

SWV = Square wave voltammetry.

TAPc = Tetraamino phthalocyanine.

TBABF₄ = Tetrabutylammonium tetrafluoroborate.

TEM = Transmission electron microscopy.

UME = Ultra-micro electrode.

UV/vis = Ultraviolet/ visible.

XPS = X-ray photoelectron spectroscopy.

XRD = X-ray diffractometer.

List of Symbols

ΔE = Peak potential separation.

$\text{\AA}$ = Angstrom

A = Electrode surface area.

C = Concentration.

C_{dl} = Double layer capacitance.

E_{pa} = Anodic peak potential.

E_{pc} = Cathodic peak potential.

F = Faraday's constant.

f = Frequency.

I_{ac} = Anodic peak current.

I_D = Intensity of Raman D band.

I_G = Intensity of Raman G band.

i_L = Limiting current.

I_p = Peak current.

I_{pc} = Cathodic peak current.

k_{app} = apparent rate transfer constant.

L_a = crystallite size.

R_{ct} = Charge transfer resistance.

R_s = Solution resistance.

T = Temperature.

ν = scan rate.

W = Warburg Impedance.

Z' = Real impedance.

Z'' = Imaginary impedance.

α = Transfer coefficient.

η = Overpotential.

λ_{laser} = laser wavelength.

ω = Rotational speed.

Γ = surface coverage.

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Chapter One: Introduction.

1. Introduction

This work discusses different ways of forming hybrid nanomaterials between multi walled carbon nanotubes (MWCNT), graphene nanosheets, and quantum dots with substituted metallophthalocyanines. The hybrid nanomaterials are examined for electrocatalysis of reactions such as oxidation of thiols, reduction of herbicides (e.g. paraquat) and oxygen reduction. The properties, methods of preparation and electrochemical characterisation, and possible applications of individual components and nanocomposite materials are discussed herein.

1.1. Overview of Phthalocyanine compounds.

1.1.1. Phthalocyanine structure.

The history of the synthesis and properties of phthalocyanines (Pcs) has been well described in literature. In brief, Pcs belong to a class of macrocyclic organic chromogen compounds which were discovered in the 1930's [1]. The structure elucidation of phthalocyanine compounds was extensively investigated by Linstead and coworkers in 1933-1934 [1]. The structural formulae for a metal-free phthalocyanine and a metallophthalocyanine are shown in Fig. 1.1.

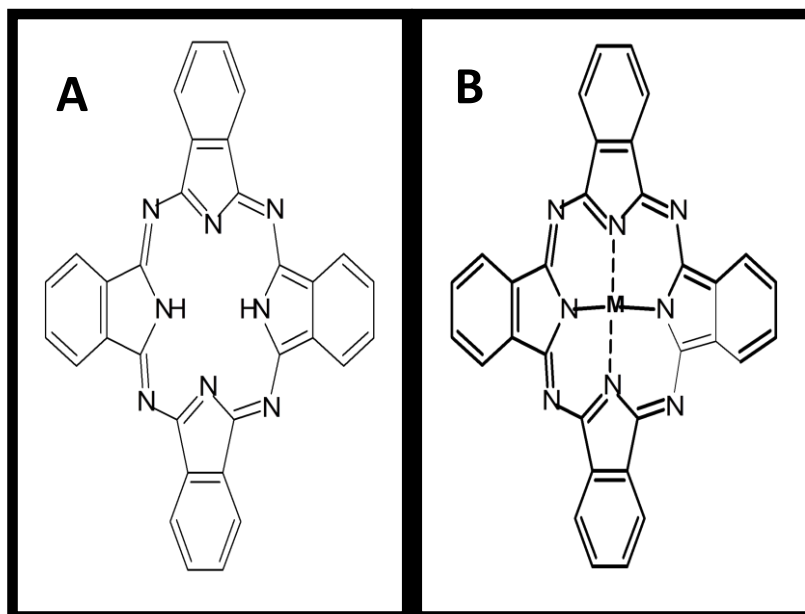


Fig. 1.1. The structural formulae for an unsubstituted metal-free phthalocyanine (A), and an unsubstituted metallophthalocyanine (B).

1.1.2. Applications of phthalocyanines (Pcs).

Phthalocyanine compounds exhibit remarkable thermal and chemical stability, and good electrical properties [1-3]. Pcs are blue/green, hence their wide use in areas such as in dyes and pigments [4]. Phthalocyanine compounds have shown some photocatalytic and electrocatalytic properties. The focus of this work is on the electrocatalytic behaviour of individual MPcs and their hybrid systems. The first reports on the catalytic properties Pc compounds appeared in the late 1930s [5-7]. Since then, metallophthalocyanines have become well known as electrocatalysts [8,9]. The focus of this work is on the electrocatalytic behaviour of derivatives of CoPc. There is a wealth of information reported on electrocatalysis of cobalt phthalocyanine and its derivatives e.g. for nitrite oxidation [10], aerobic oxidation

of secondary alcohols to make ketones [11], reduction of carbon dioxide [12], and sulfhydryl oxidation [13], among others. Studies show that CoPc and its derivatives are good candidates for the design of smart platforms for electrochemical sensing or oxygen reduction reaction (ORR) electrocatalysis.

1.1.3. Metallophthalocyanine spectra.

The schematic representation of energy levels of electronic and charge transfer transitions in a metallophthalocyanine complex are depicted in Fig. 1.2. The scheme shows the origins of the Q and B bands in the electronic spectrum of MPcs shown in Fig. 1.3. Both Q and B bands arise from the π - π^* transitions depicted in Fig. 1.2, i.e. the intense Q band arises from $a_{1u} \rightarrow e_g$ and the B bands arise from $a_{2u} \rightarrow e_g$ and $b_{2u} \rightarrow e_g$ transitions [14].

The superimposition of the two B bands (B_1 and B_2) results in a characteristic broad B band in the UV-vis spectra of phthalocyanines, Fig. 1.3. The charge transfer bands can also be observed between the Q and B bands but do not frequently occur in most MPcs. UV/Vis spectra were employed in this work to characterize synthesized CoPc complexes and the effects of nanomaterials on the spectra.

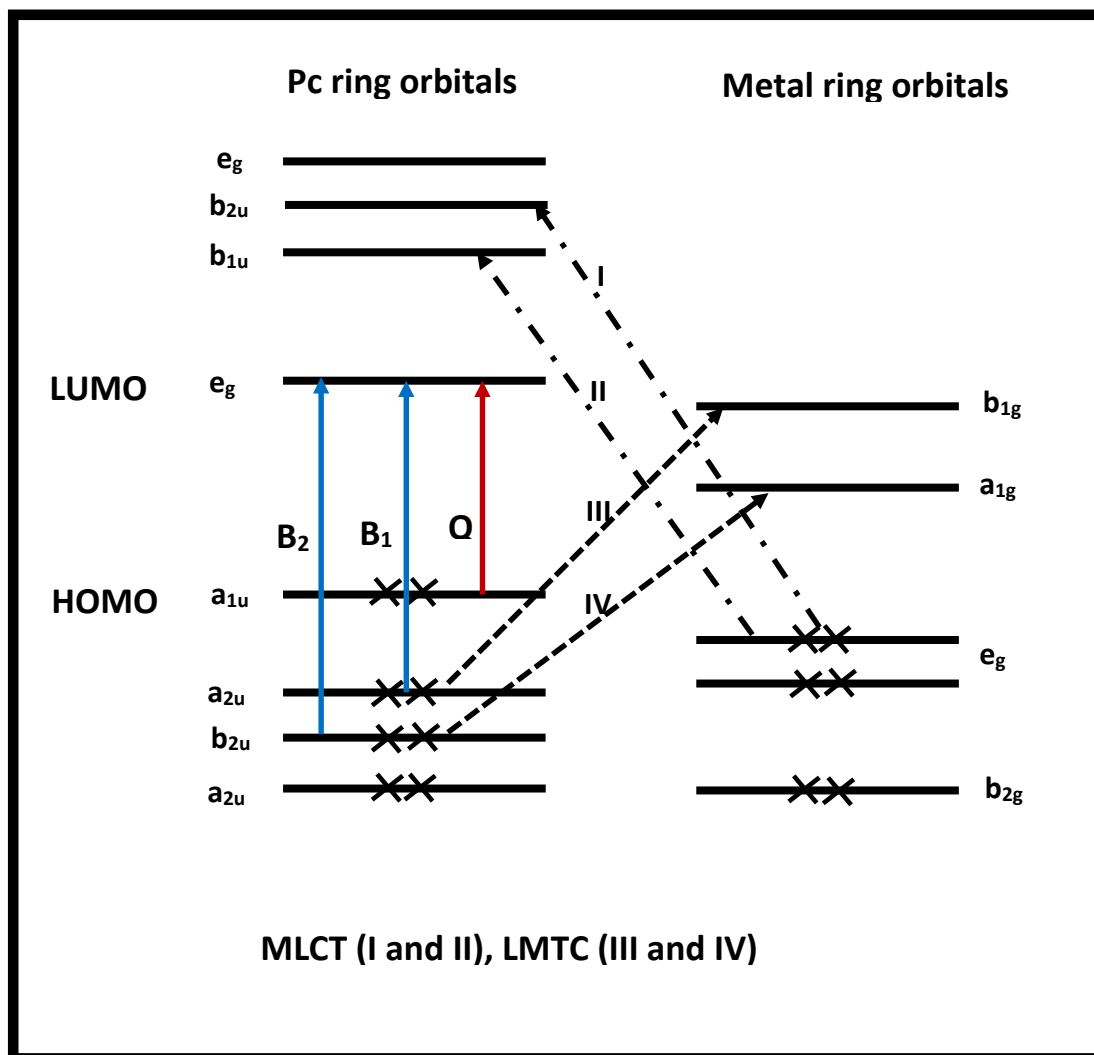


Fig. 1.2. Electronic and charge transfer transitions in a Pc showing the origins of Q and B absorption bands. MLCT = Metal-to-ligand charge transfer, LMCT = Ligand-to-metal charge transfer.

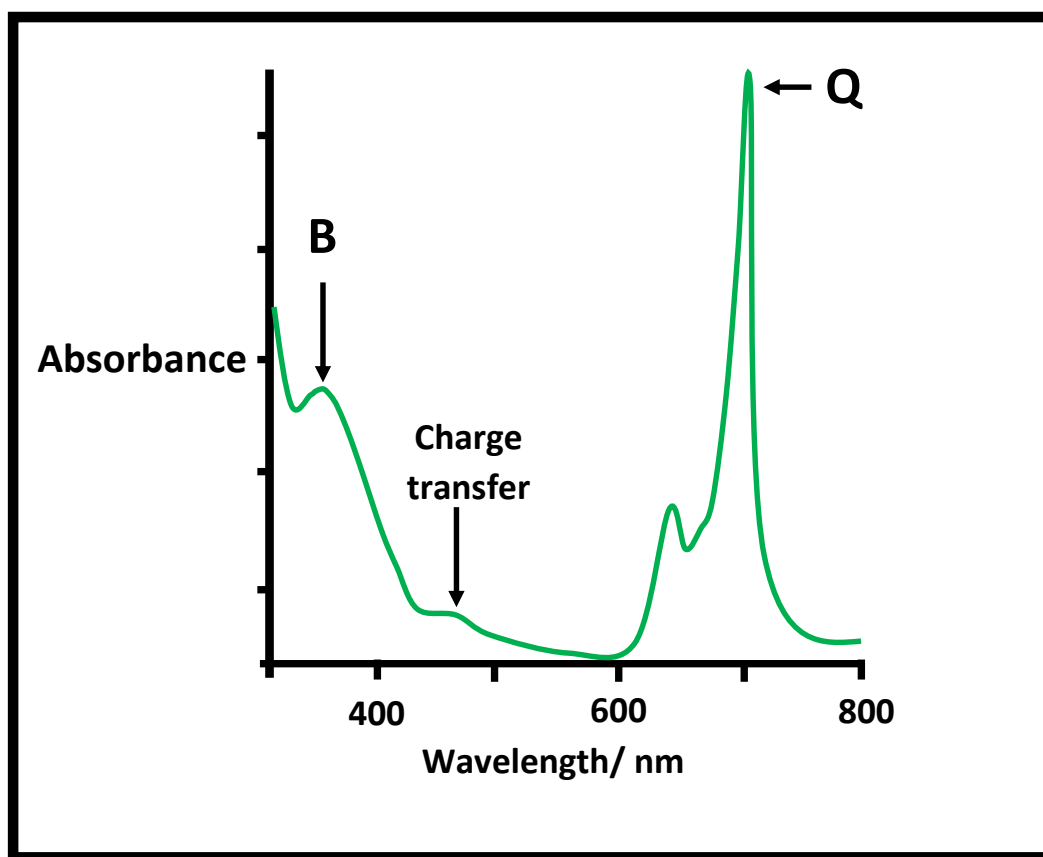


Fig. 1.3. Electronic absorption spectrum showing common absorption bands in MPcs.

1.1.4. Phthalocyanines used in this thesis.

Two different metallophthalocyanines (MPcs) i.e. (i) tetra (4-(4,6-diaminopyrimidin-2-ylthio) phthalocyaninato cobalt (II) (CoPyPc) (Fig. 1.4A) (ii) cobalt tetraamino phthalocyanine (CoTAPc) (Fig. 1.4B), are used in this work. CoTAPc was selected because of its well-known electrocatalytic properties [15-20], making it easier for the characterisation of its new hybrid systems fabricated in this work. CoPyPc is synthesized in this work for the first time. The preference for synthesizing a new CoPyPc in this work instead of the commonly used CoTAPc is as a result of the bulkier substituents for the former which reduces aggregation. In addition CoPyPc has more

NH₂ groups, hence more polymerization points when compared to CoTAPc. The sulphur-linkage in CoPyPc is electron donating which will result in ease of oxidation, hence improved electrocatalytic activity for oxidation. The new CoPyPc has been further tuned into two different forms i.e. it has been polymerized (poly-CoPyPc) and doped with iodine (doped-CoPyPc). Both the polymeric and doped forms of CoPyPc have been characterized for their electrocatalytic properties as individual catalysts or nanohybrid catalysts.

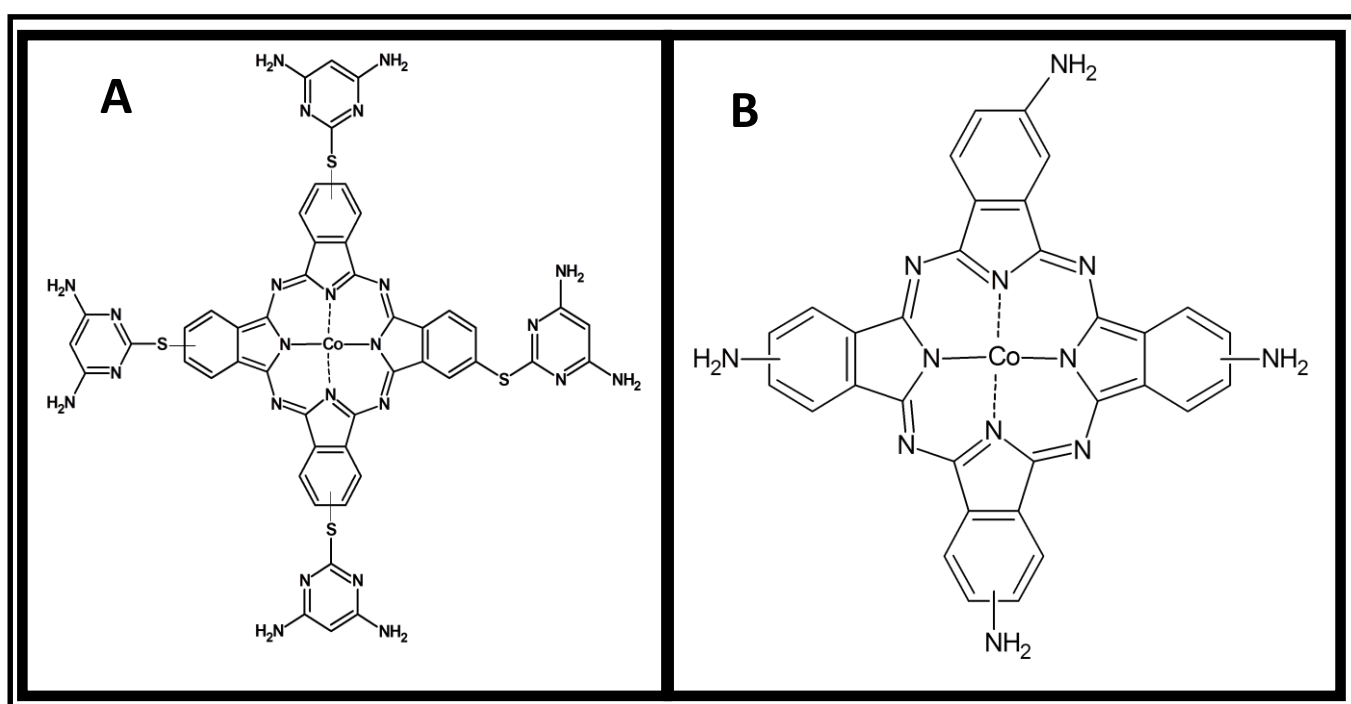


Fig. 1.4. Structures of monomeric MPCs used in the fabrication of nanocomposites in this work; CoPyPc (A), CoTAPc (B).

1.2. Overview of Quantum dots (QDs).

QDs are semiconductor nanoparticles with unique photophysicochemical properties and functions. They exhibit strongly size dependent optical and electrical properties

[21]. QDs have found applications in fields such as optical sensing, chemiluminescence detection, and photoelectrochemical bioanalysis [22, 23]. The properties of QDs result from quantum-size confinement, which occurs when metal and semiconductor particles are smaller than their exciton Bohr radii (about 1 to 5 nm). Although QDs have been mainly used because of their photophysical behaviour, there have been reports on their electrochemical properties [24]. In this work, QDs have been selected to act as spacers/ intercalating agents to prevent agglomeration or restacking of reduced graphene nanosheets (rGNS) during electrode modification for electrocatalysis. Aggregation of the QDs is also prevented. Due to the nanometer size of QDs, they can embed well in between graphene nanosheets. Furthermore, the use of QDs intercalators in electrocatalytic reactions is not well reported and this is the first time that CdSe QDs are used as intercalators between GNS for the ORR electrocatalysis, Fig. 1.5.

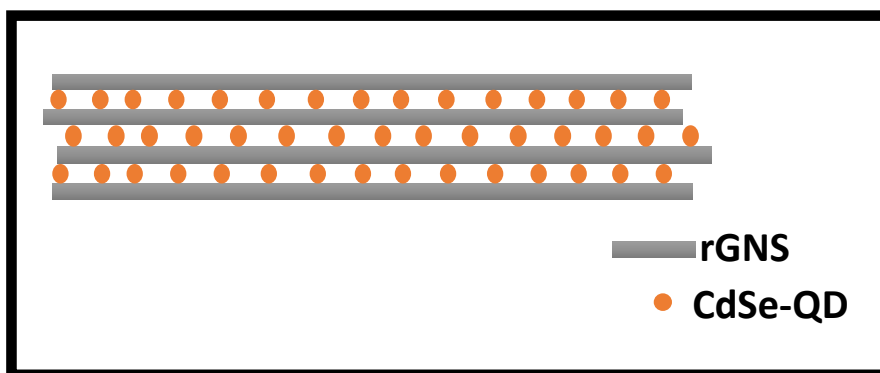


Fig. 1.5. A schematic representation of a nanocomposite of rGNS-CdSe-QD nanocomposite.

QDs on their own have been used for electrode modification and detection of DNA or proteins [23]. QDs enhance the electrocatalytic activity of Pc for detection of analytes such as chlorophenols [25]. Table 1.1 gives some examples of

electrocatalytic applications of QDs [23, 25-28]. As Table 1.1 shows, there are only a few examples of Pc-QDs used for any electrocatalysis. QDs have been mainly used in fluorescence applications.

Table 1.1: Some known electrochemical applications of QDs.

QDs/QDs-nanocomposites	Electrode modification	Application	Ref.
CdS	Layer-by-layer deposition on gold electrode	DNA detection	[23]
CdTe-QDs-NiTAPc	Adsorption through drop-drying on gold electrode	Chlorophenols detection	[25]
[CdS: ZnS: CuS: PbS]-QDs-Aptamer	Immobilization on gold electrode	Lysozyme and thrombin detection	[26]
Silicon nanocrystals QDs	Unmodified Pt electrode	Optoelectronic sensing of radicals	[27]
CdTe QDs/CNT	Adsorption on GCE	Glucose sensing	[28]

NiTAPc: nickel tetraamino phthalocyanine.

Furthermore, Table 1.1 shows that CdSe-QDs alone or with MPcs have not been used for ORR detection; hence employed for the first time in this work for this application on a reduced graphene nanosheet platform.

1.3. Carbon nanomaterials and their hybrid nanocomposites.

1.3.1. Multi-walled Carbon Nanotubes (MWCNTs) nanocomposites.

MWCNTs are preferred over single walled carbon nanotubes (SWCNTs) in this work since studies have shown that the presence of the former results in better catalytic activity in terms of reduced cathodic to anodic peak separations [29]. The early discovery of carbon nanotubes (CNTs) in 1952 was through the work of Radushkevich and Lukyanovich [30]. However, much attention on their applications grew after a report by Iijima in 1991 [31]. MWCNTs were observed as tubes consisting of two or more seamless graphene cylinders concentrically arranged, with an innermost tube of 2.2 nm in diameter [31]. The concentric nanotubes are held together by secondary, van der Waals bonding [32]. MWCNTs tend to have diameters in the range 2 - 100 nm and an inner layer spacing of the graphitic microtubules of 0.3 nm - 0.4 nm. A representation of MWCNTs is shown in Fig. 1.6. Since their discovery, these helical microtubules of graphitic carbon have become a centre of focus by many researchers who have reported on a number of their unique properties such as remarkable physical and mechanical properties, chemical and thermal stability, and superior current carrying capacity [33], among others. The nanometer size of MWCNT provides good dispersion and high surface area features. This is very important in reducing catalyst loading hence making MWCNTs to be suitable electrocatalytic support systems for improving performance of metallophthalocyanines for applications in fabrication of miniaturized sensor platforms. It is out of these unique properties that a wide range of applications for MWCNTs have evolved; such as in field emission displays [34], microelectronic

devices [35], scanning probe microscopy [36], electrocatalysis and electrochemical sensing [37-40].

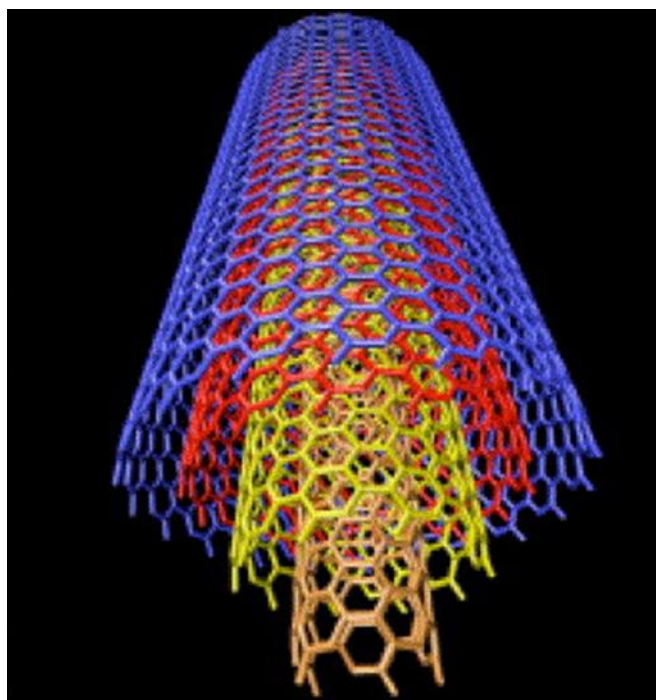


Fig. 1.6. Schematic representation of MWCNTs [41].

The interest in using nanocomposites containing phthalocyanines and MWCNTs in this work is influenced by the fact that nanocomposites (not containing phthalocyanines) have also been reported to enhance electrocatalytic responses in many applications such as glucose sensing [42], NADH oxidation [43], ORR in fuel cells [44], lithium battery application [45], etc. In this work, MWCNT are used as (i) non-oriented GCE modifiers, (ii) MWCNT-metallophthalocyanine nanocomposite GCE modifier, and (iii) intercalating/spacing agent for reduced graphene nanosheets to prevent their re-stacking during modification by adsorption. Table 1.2 shows that MWCNT alone or with Pcs have been used for electrode modification [46-71].

Table 1.2. Examples of MWCNTs or graphene materials and their nanocomposites used in electrode modification.

Electrode modifier	Electrode	Method of Modification	Analyte	Ref.
NiPcNPs/MWCNT	BPPGE	Adsorption	Asulam pesticide	[46]
MWCNT	BPPGE	Adsorption	Asulam pesticide	[46]
CoPc/MWCNT-silk fibroin	GCE	Adsorption	Bisphenol A	[47]
CoPc/MWCNT	GCE	Adsorption	Ascorbic acid	[48]
MWCNT	GCE	Adsorption	Ozone	[49]
Carbon black NPs-graphene	Nickel form substrate	Adsorption	KOH electrolyte only	[50]
Graphene/Fe ₂ O ₃ /SnO ₂	Graphene/Fe ₂ O ₃ /SnO ₂	No electrode modification	LiPF ₆ electrolyte	[51]
Graphene-Pt	RDGCE	Adsorption	Methanol	[52]
MWCNT/graphene	GCE	Adsorption	Tyrosine and paracetamol	[53]
β-CoTSPc/MWCNT	GCE	Electrodeposition/adsorption	Epinephrine	[54]
CoPc/MWCNT	GCE	Adsorption	ORR	[55]

CoPc/MWCNT, CuPc/MWCNT	Glass/quartz plates	Adsorption	H ₂ O ₂	[56]
CoPc/MWCNT	GCE	Adsorption	ascorbic acid	[57]
CoPc/MWCNT	GCE	Adsorption	carbaryl	[58]
FePc/ MWCNT	GCE	Adsorption	ORR	[59]
CoPc/MWCNT	CPE	CPE	guanine	[60]
CoPc/ MWCNT/PAMAN	GCE	Adsorption	virus biosensor	[61]
FeOBSPc/MWCNT and CoOBSPc- MWCNT	EPPGE	Adsorption	ORR	[62]
CoPc/ MWCNT	GCE	Adsorption	phenolic compounds	[63]
FePc/MWCNT/ PEDOT	SPE	Adsorption	nitrite	[64]
FePc/MWCNT	CPE	CPE	dopamine (serotonin present)	[65]
CoTtBPc/MWCNT	GCE	Adsorption	ORR	[66]

Nafion/GOD/poly-NiTSPc/MWCNT	GCE	Electropolymerization / adsorption	glucose biosensor	[67]
PtFeOCPc-MWCNT	EPPGE	Adsorption	ORR	[68]
CoPc/FePc/rGO	GCE	Adsorption	ORR	[69]
PAMAM-NT-NiTSPc	ITO-coated glass electrode	LBL deposition	Dopamine	[70]
FePc-MWCNTs and Co(Bu)Pc-MWCNTs	GCE	Adsorption	ORR	[71]

NPs = Nanoparticles, MWCNT = multiwalled carbon nanotubes, RDGCE = rotating disk glassy carbon electrode, GCE = glassy carbon electrode, TSPc = tetrasulphophthalocyanine, PAMAN = poly(amido amine), OBSPc = octabutylsulphonyl phthalocyanine, PEDOT = poly(3,4-ethylenedioxythiophene), TtBPc = tetra-tert-butylphthalocyanine, GOD=glucose oxidase, Basal plane pyrolytic graphite electrode = BPPGE, CPE = carbon paste electrode, SPE = screen printed electrode, rGO = reduced graphene oxide, EPPGE = edge plane pyrolytic graphite electrode, ORR = oxygen reduction reaction, OCPc = octacarboxy phthalocyanine, ITO = indium-tin oxide, LBL = layer-by-layer.

The data in Table 1.2 is for when the individual nanomaterials are mixed prior to modification of the electrode.

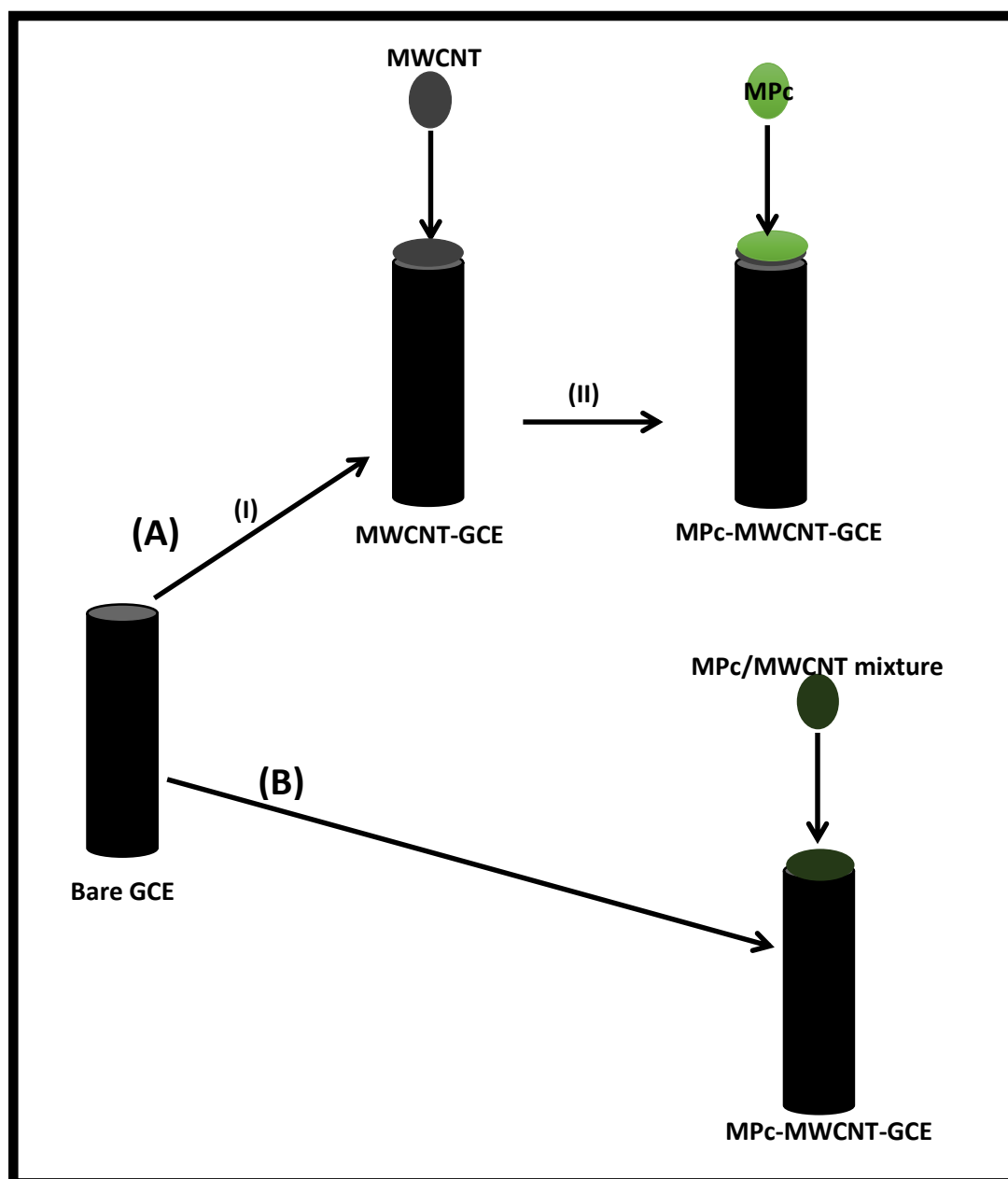


Fig. 1.7. A schematic representation of the preparation of nanocomposites of MPc and MWCNTs using sequential drop-drying (A), and premixing and drop-drying (B) procedures.

Since the method of modifying the electrode surface is crucial in influencing the electron transfer processes, this work gives a comparative study of drop drying a premixed MPc and MWCNTs suspension against the sequential drop dry MPc-MWCNTs

modified surface, whereby a drop of MWCNTs is placed on the GCE surface, followed by the addition of a drop of MPc on top of the MWCNTs layer, as illustrated in Fig. 1.7.

This work shows that the catalytic behaviour is improved when MWCNT are placed first on the electrode surface and followed by MPc on top, and less activity was observed when the MPc was placed directly on to the electrode surface followed by MWCNTs. Fig. 1.8, shows the representation of the nanocomposite of the step by step (sequential) modification as opposed to just mixing. Since MWCNT have been used in electrocatalysis and have good conductivity properties [72-74], combining the two electrocatalysts, CoPc derivatives and MWCNT is expected to enhance electrocatalytic activity by a synergistic effect.

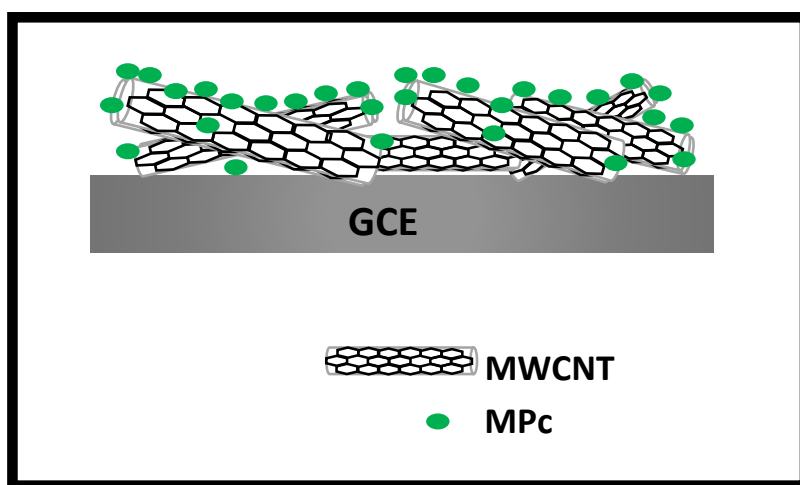


Fig. 1.8. A schematic representation of an MPc/MWCNT hybrid nanocomposite on GCE.

Thin films of electroactive MPcs on solid electrode surfaces have been fabricated by different pathways including adsorption [9,75], electropolymerization [76-78] and click chemistry [79] to name just a few. In this work, an electrocatalytic

nanocomposite platform has been fabricated from poly-MPcs and MWCNT in two steps: (i) drop-drying MWCNTs on a GCE and (ii) separate electropolymerisation of each of the two cobalt phthalocyanine derivatives (CoTAPc and CoPyPc), Fig. 1.9. Polymerization is more reliable than adsorption and the thickness of the film can be controlled by the number of polymer cycles. Hence this work reports on the polymerization of CoPc derivatives onto MWCNT and evaluation of their electrocatalytic activity. CoPyPc has two polymerizable groups on the substituent and X-ray photoelectron spectroscopy (XPS) is used to confirm the point of polymerization. The electrocatalytic activities of the adsorbed and polymerized complexes are compared in this work. Electropolymerisation of CoTAPc on electrode surfaces is well-known [15,76-78] but its electropolymerisation on a MWCNT platform for electrocatalysis has not been reported.

Carbon electrodes are effective at adsorbing materials with extended π -conjugated systems such as MPcs and CNTs, hence the selection of the GCE in this work. The modified electrodes are employed in the detection of l-cysteine and the results are compared to when CoPc derivatives are adsorbed rather than polymerized. The effect of MWCNT on the electrocatalytic effect is also evaluated. It is the first time the electropolymerized form of a phthalocyanine is made into a nanocomposite with MWCNT (Fig. 1.9) for electrocatalysis. This work also reports for the first time, the combination of MWCNT, reduced graphene and MPc for electrode modification. MWCNTs reduce agglomeration of graphene nanosheets (hence large electrocatalytic surface area) whilst the former also further enhance the electron transfer activity for the electrocatalytic process occurring at the MPc on the surface. The resultant

behaviour is fast electron transfer, improved sensitivity and very low limits of detection (LODs).

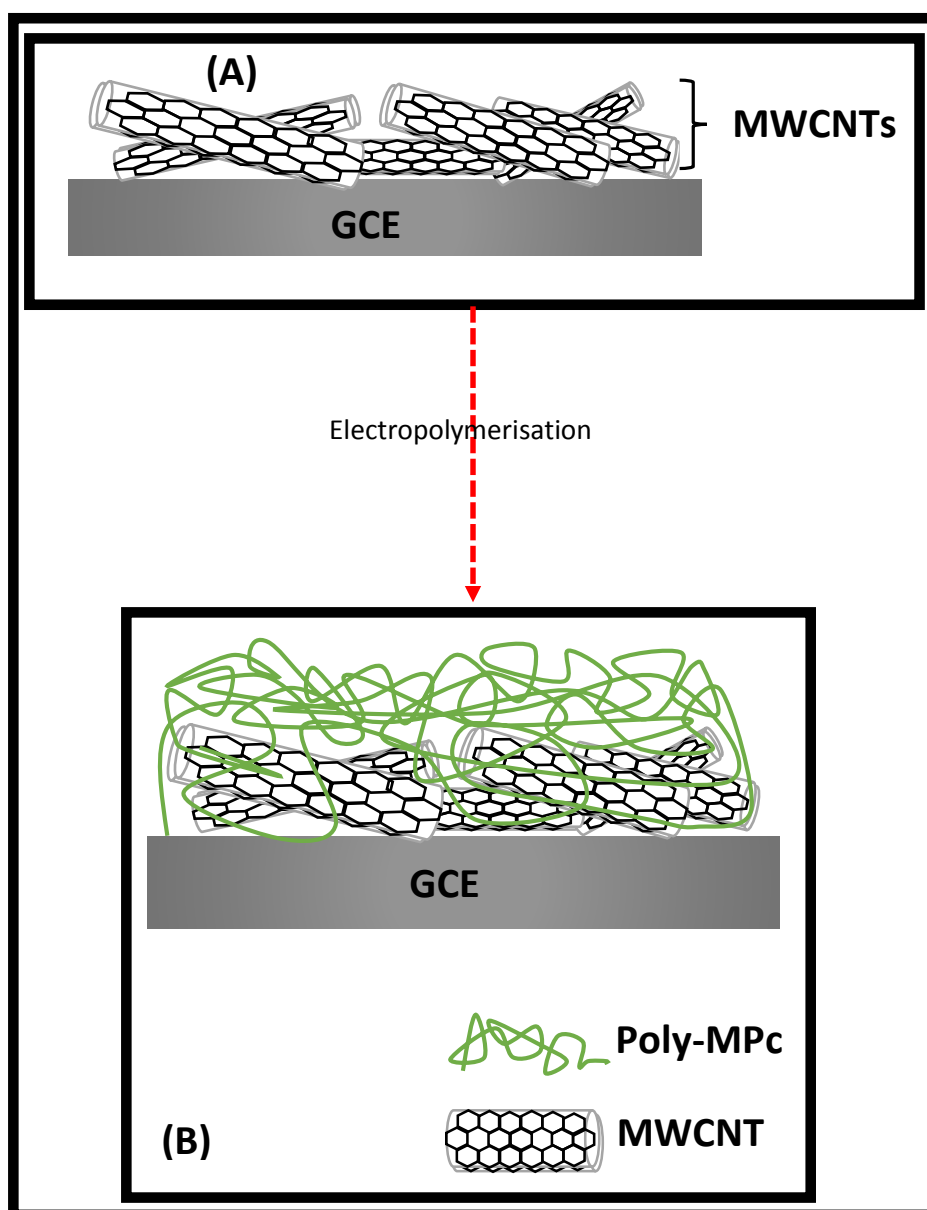


Fig. 1.9. A schematic representation of the preparation of poly-MPc-MWCNT nanocomposite on GCE.

1.3.2. Graphene Nanocomposites.

Graphene oxide nanosheets (GONS) were reduced to improve on the graphitic sp^2 carbon network that enriches the conjugation system for efficient electron transfer.

Thus, reduced graphene nanosheets have recently drawn increasing attention as novel carbon nanomaterials due to their outstanding electronic, thermal, mechanical and chemical properties, high surface area and broad electrochemical window [80-90]. However, graphene nanosheets can undergo π -stacking through van der Waal's interactions [91,92], thereby reducing the available active surface area for applications such as in electrocatalysis. A possible route to harness outstanding properties of graphene nanosheets for practical applications is to make nanocomposites by incorporating some nanomaterials into the graphene sheets, which will inhibit the agglomeration and improve the electrode conductivity [50].

Graphene nanosheets-polystyrene and graphene nanosheets-polyaniline nanocomposites have been reported and were found to display high electrical conductivity and good tensile strength [93,94]. Carbon-black nanoparticles were used as spacers for graphene nanosheets and the electrochemical performances of hybrid materials were found to be superior compared to pure graphene material [50]. Fe_2O_3 and SnO_2 were dispersed on graphene to reduce their restacking and improve the electrochemical performance of Li-ion batteries [51]. GNS-Pt electrocatalyst composites have shown unusually high activity towards methanol oxidation relative to Pt-carbon black catalyst [52]. GNS- Al_2O_3 composites have also been reported to have better electrical conductivity than individual GNS [95]. Therefore, this work envisages the design of a smart platform for fabrication of a nanocomposite electrocatalyst containing MWCNT and reduced graphene nanosheets, Fig. 1.10.

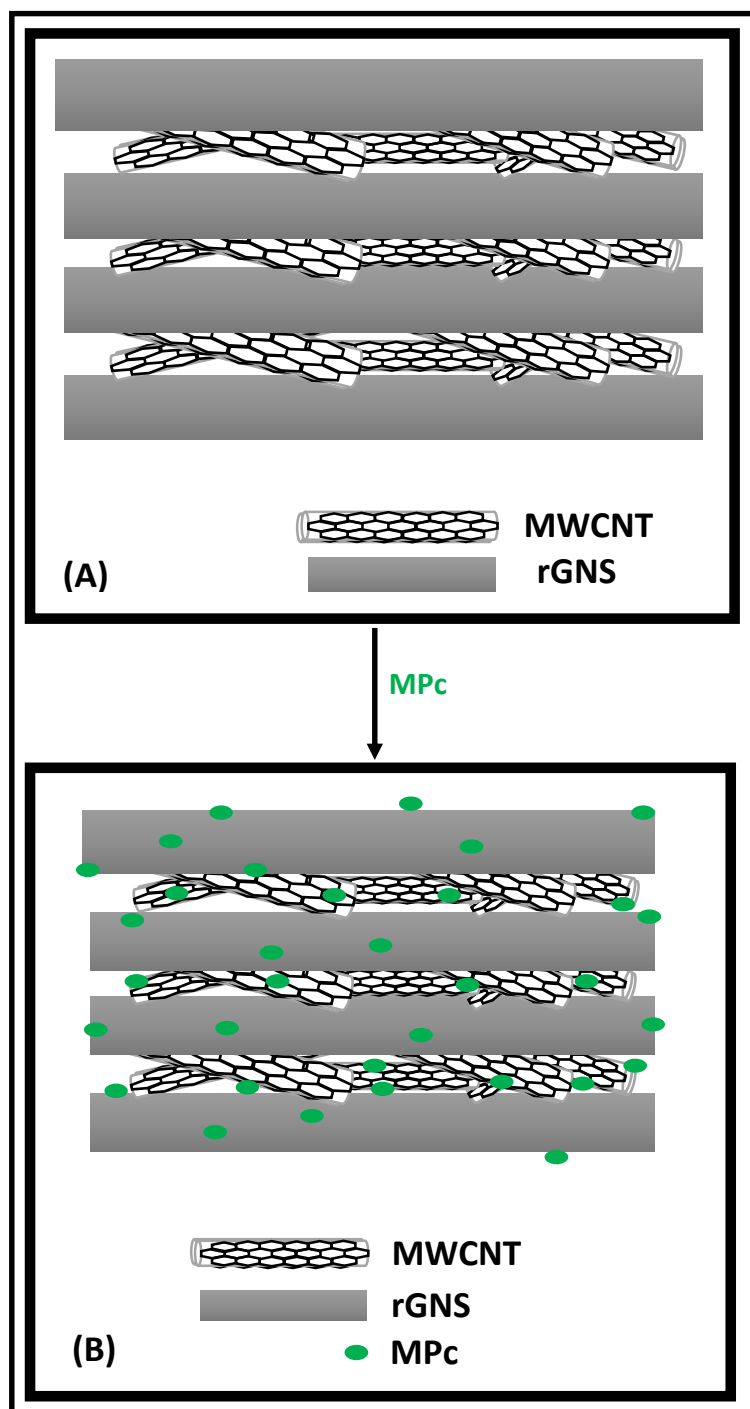


Fig. 1.10. A schematic representation of a nanocomposite of MWCNT intercalated reduced graphene nanosheets in the absence (A) and in the presence (B) of MPc molecules.

This is the first time that MWCNT are used as spacers for rGNS in the presence of a MPc for electroreduction. The advantages of using MWCNTs instead of the spacers described above, is the fact that MWCNTs have high electrical conductivity and good thermal and chemical stability; making the nanocomposite suitable for applications such as in high temperature and reactive chemical environments.

In this work, the MWCNT-rGNS nanocomposites are decorated with metallophthalocyanine (CoTAPc) because of its well-known electrocatalytic behaviour towards detection of herbicides [96,97]. A herbicide, paraquat (N, N'-dimethyl-4,4-bipyridiliumdichloride), is used as a test molecule to demonstrate the effect of the presence of MWCNT and reduced graphene nanosheet on the electrocatalytic performance of CoTAPc. Table 1.3 lists all the Pc containing nanocomposites used in this work.

Table 1.3. A summary of all Pc nanocomposite electrocatalysts used in this work. The catalytic behaviour was investigated on a GCE.

Catalyst	Application
CoTAPc-MWCNT(sequential)	l-cysteine electrooxidation
CoTAPc-MWCNT(premixed)	l-cysteine electrooxidation/ PQ reduction
CoTAPc	PQ reduction
CoTAPc-rGNS-2 (sequential)	PQ reduction
CoTAPc-MWCNT (sequential)	PQ reduction
CoTAPc-rGNS-2-MWCNT (sequential)	PQ reduction
CoPyPc	ORR
CoPyPc-rGNS-2 (sequential)	ORR
CoPyPc	ORR/ l-cysteine electrooxidation
CoPyPc-rGNS-2 -CdSe QDs (sequential)	ORR
CoPyPc-MWCNT (covalently linked)	ORR/ l-cysteine electrooxidation
CoPyPc-MWCNT-COOH (mixed)	ORR/ l-cysteine electrooxidation
Iodine doped CoPyPc	ORR
Iodine doped CoPyPc-MWCNT(sequential)	ORR
Iodine doped CoPyPc	ORR

Iodine doped CoPc	ORR
CoPc	ORR
Poly-CoTAPc-GCE	l-cysteine electrooxidation
Poly-CoTAPc-MWCNT-GCE	l-cysteine electrooxidation
Poly-CoPyPc-GCE	l-cysteine electrooxidation
Poly-CoPyPc-MWCNT-GCE	l-cysteine electrooxidation

1.3.3. Iodine-doped Cobalt Phthalocyanine-MWCNT nanocomposite.

Metallophthalocyanines, as previously described, are well known electrocatalysts for many reactions including ORR [9,11,98,99]. However in their application in ORR activity, MPcs may suffer from chemical destruction by H_2O_2 produced as either an intermediate product for a 4-electron system or final product for a 2-electron system during oxygen reduction. Tuning the substituents of the metallophthalocyanines can result in changes in their physicochemical properties which might lead to enhanced electrocatalytic activity towards ORR and greater stability in H_2O_2 environment. Doped nanocomposites appear to be one way that can be used to improve on ORR electrocatalysis [100-107]. Some metallophthalocyanine derivatives were found to have improved conductivity upon iodine-doping [108,109]. Apart from one study [110] using iodine doped unsubstituted cobalt phthalocyanine (CoPc), oxygen reduction using iodine doped phthalocyanines has not been explored. Hence in this work, CopyPc was doped with iodine to promote electron transfer. As highlighted

above, MWCNTs have been used to promote electron transfer properties of phthalocyanines [46-48,111,112], hence are employed in this part of work in combination with iodine doped CoPyPc. There are no reports which combine both iodine doped Pc and MWCNTs, even though the advantage of the combination is beneficial for improved electron transfer. The individual components (CoPyPc and iodine doped CoPyPc) and when adsorbed on MWCNT were used for the modification of a glassy carbon electrode (GCE) and used for ORR for the first time.

1.3.4. Nanocomposites from covalently linked and mixed MWCNT-COOH and CoPyPc.

The method of preparing the nanocomposite has a strong influence on its catalytic performance. Another set of nanocomposite electrocatalysts were prepared in this work to modify solid electrode surfaces with an overriding intent of facilitating some rather sluggish reactions occurring at the bare surfaces. The nanocomposites were fabricated by functionalizing MWCNT with carboxylic acid functional groups and covalently linking to the amine terminals of CoPyPc, Fig. 1.4A. CoPyPc was chosen due to the presence of a number of NH_2 groups for linking to acid functionalized MWCNTs. Pcs have been covalently linked to single walled carbon nanotubes (SWCNTs) for electrocatalytic applications [97,113], but there are no reports on its covalent coordination to MWCNTs. Thus, MWCNTs are covalently linked to CoPyPc, the resulting conjugate is characterized and its electrocatalytic activity is examined in comparison with when CoPyPc is adsorbed onto MWCNTs without a chemical bond. The electrocatalytic activities of the conjugates are also tested for the oxidation of L-cysteine as a test analyte.

1.4. Target/ test analytes in this work.

The analytes used in this work to test the possible application of the nanocomposites in electrocatalysis are l-cysteine, paraquat and oxygen. The structures of l-cysteine and paraquat are shown in Fig. 1.11.

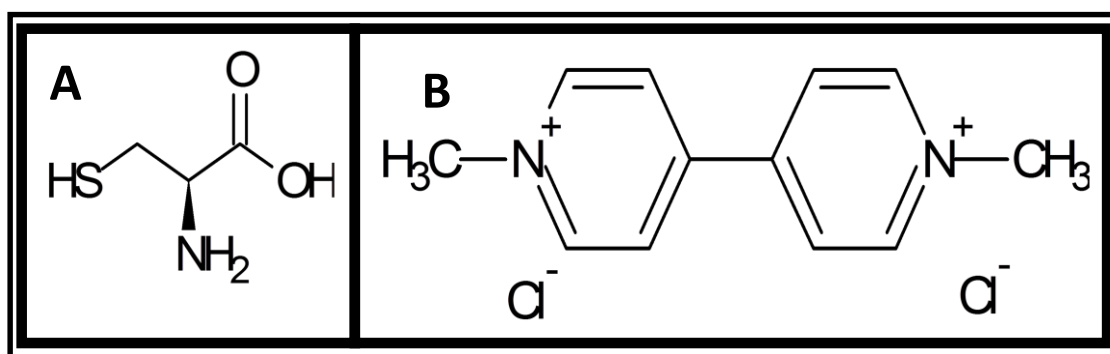


Fig. 1.11. Structures of l-cysteine (A) and paraquat (B) used as test analytes in this work.

1.4.1. Thiols: L-cysteine electrooxidation.

L-cysteine is a well-known thiol containing amino acid which is found in many peptide and protein molecules. This is because L-cysteine is nucleophilic and is readily deprotonated under physiological conditions hence exist in cells in the form of reactive thiolate ions, thereby enabling it to be readily involved in crucial biological functions such as protein folding [114]. It has also evolved that the levels of l-cysteine in tissue or physiological fluids such as blood is linked to specific pathological conditions or human diseases such as lung cancer, mental conditions, cardiovascular diseases, gastrointestinal tract tumors, genitourinary, diabetes, kidney and musculoskeletal problems, depigmentation of hair, lethargy, retarded growth in children [115-117] etc. It is against this background that many researchers

have tried to develop protocols for monitoring physiological levels of thiols [118-120]. Hence, l-cysteine is used as a test analyte in this work. L-cysteine has been analysed on Pcs alone [9] but not on nanocomposites until this work.

1.4.2. Herbicide: Paraquat (PQ) electroreduction.

Due to increasing world demand for food, there has been an increasing application of agrochemicals to prevent crop losses before and after harvest. These chemical toxins are usually indiscriminate in their mode of action, and are toxic at trace levels; hence pose a serious risk up the food chain especially to human health. It is therefore of primary importance to monitor the levels of these toxins in the environment. A herbicide, paraquat (PQ) (N, N'-dimethyl-4,4'-bipyridilium dichloride) is used as a test molecule, to demonstrate the catalytic effect of the nanocomposite reported in this work on its electroreduction. Paraquat has been chosen in this work because it has been reported to be of toxicological class I i.e. it is an extremely hazardous herbicide [121] yet one of the most currently used especially in developing countries despite the fact that it has been banned in some other developed countries. Currently, the use of nanocomposites for PQ electroanalysis has not been a common practice.

1.4.3. Oxygen Reduction Reaction (ORR) electrocatalysis.

ORR has applications in fuel cells. Fuel cells electrochemically convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants [122,123]. A schematic presentation of a Proton Exchange Membrane (PEM) fuel cell is shown in Fig. 1.12.

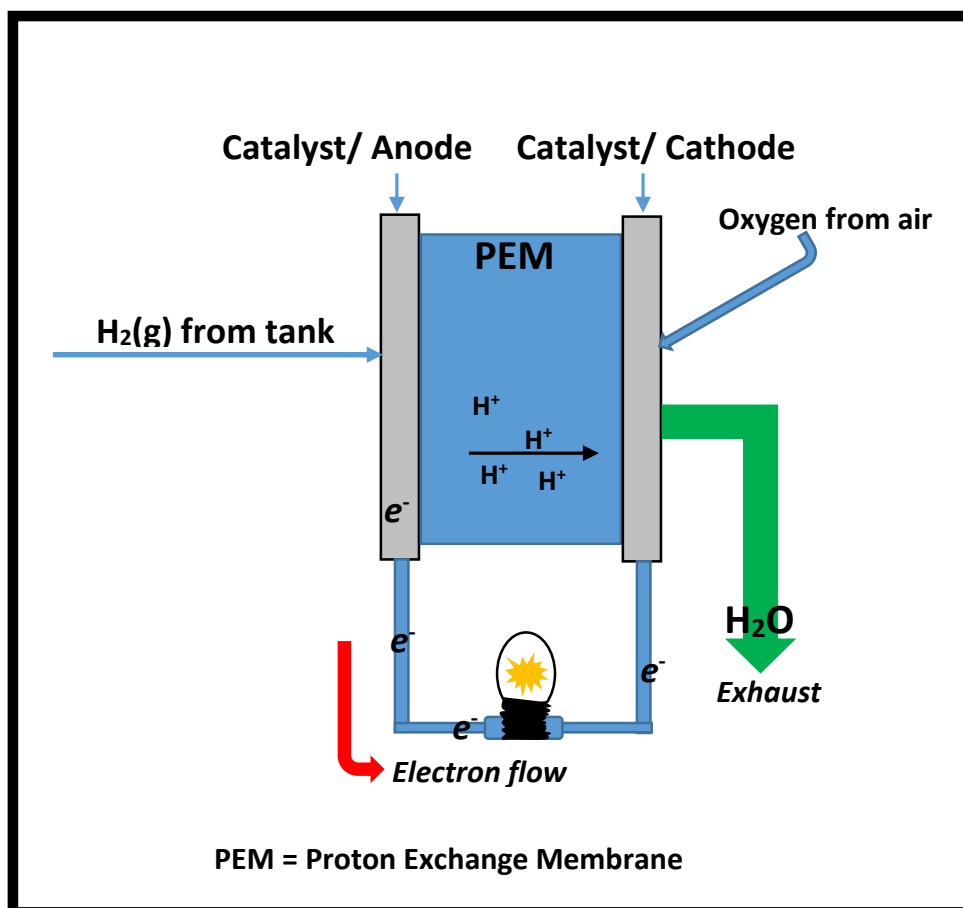


Fig. 1.12. A schematic representation of fuel cell.

Two important processes are significant for the mode of operation of such electrochemical cells i.e. anodic oxidation of the fuel and cathodic reduction of oxygen. The rate determining process for the overall performance of the fuel cell is the kinetics of the sluggish oxygen reduction reaction at the cathode. Currently, Pt-based catalysts are being used to promote ORR in fuel cells. These precious Pt-based catalysts bring a lot drawbacks especially with commercialization e.g. (i) high cost and scarcity of Pt makes it difficult for widespread application, (ii) suffer greatly from the crossover effect which results in serious decrease in fuel efficiency, and (iii) not suppressing the overpotential. High overpotential implies high energy losses in the form of heat. With these challenges at hand, it is imperative to seek non-precious ORR electrocatalysts which are highly electroactive and resistant to

crossover effect for the development of alternative cheap fuel cell prototypes. These should show minimum overpotential and good electron transfer properties.

The ideal case in ORR reaction is when the Fermi level of the electrode/catalyst is equal to the partially filled orbitals of molecular oxygen (Fig. 1.13) i.e. a situation where the overpotential is zero. However, due to kinetic limitations, overpotential always arises, Fig. 1.14. High overpotential results in slow reaction and generation of too much heat, hence the need for development of ORR catalyst platforms with improved performance.

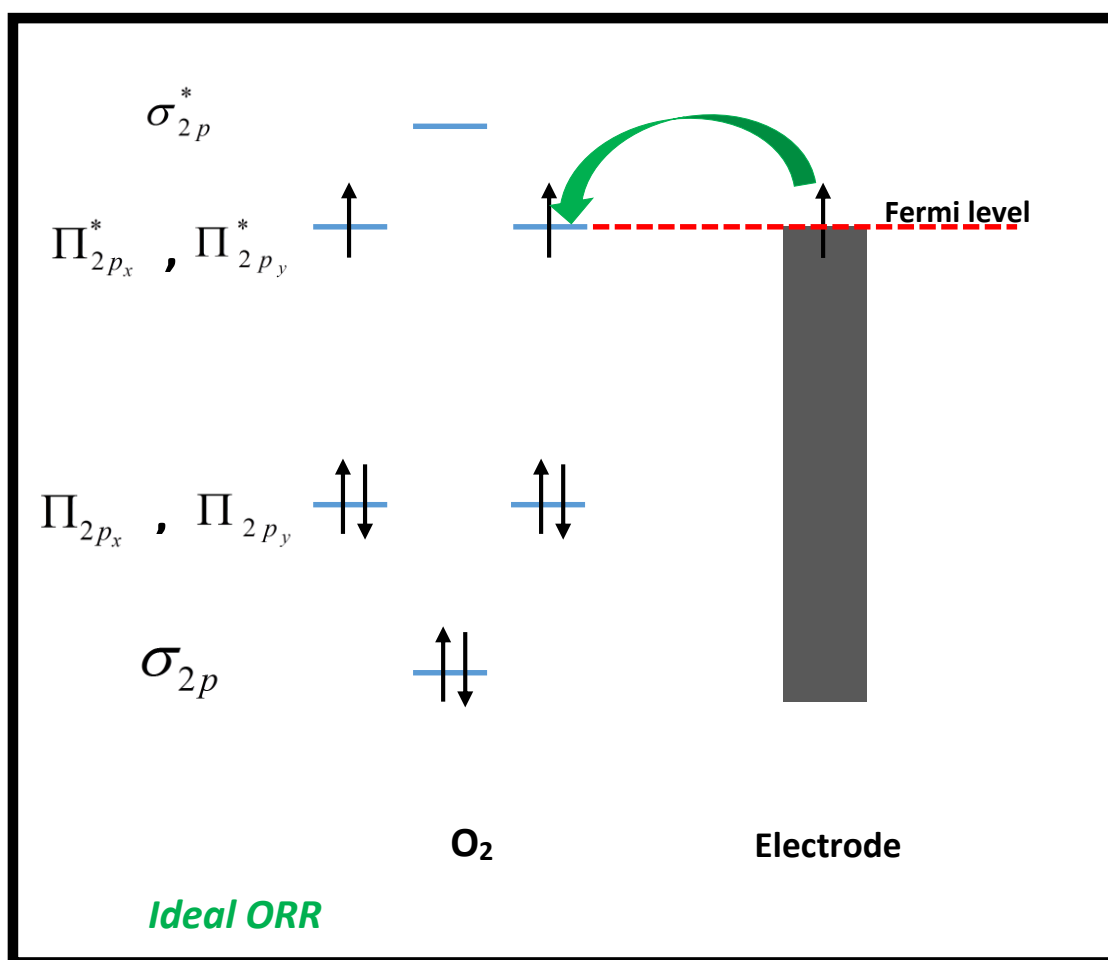


Fig. 1.13. A schematic representation of energy levels for an ideal ORR.

Furthermore, graphene and its derivatives have found considerable attention in electrocatalytic applications for ORR in fuel cells [124-131]. As stated above, the electrochemical utilisation of graphene for some potential novel applications is hindered by the tendency of its individual sheets to agglomerate. In this work, the use of QDs as intercalating agents for improving electrochemical properties of graphene nanosheets, Fig. 1.5, has been explored. This work reports for the first time on the preparation and electrochemical characterization of a nanocomposite containing QDs, rGNS and a MPc for application in ORR.

In addition to inhibiting graphene nanosheets agglomeration, QDs may also aid electron transfer. The rGNS/CdSe QDs conjugates as well as the individual components (alone or after adsorption of MPc) have been used for the modification of a GCE for ORR as a test since its detection using phthalocyanine alone is well known [132,133].

The aim of this part of work is to show the effects of combination of r-GNS-CdSe QDs on the catalysis of the ORR compared to metallophthalocyanine alone. The nanocomposite has also been subjected to methanol to test for methanol crossover effect (the effect of diffusion of methanol from the anode to the cathode through the membrane) which can lead to sluggish electron transfer at the cathode.

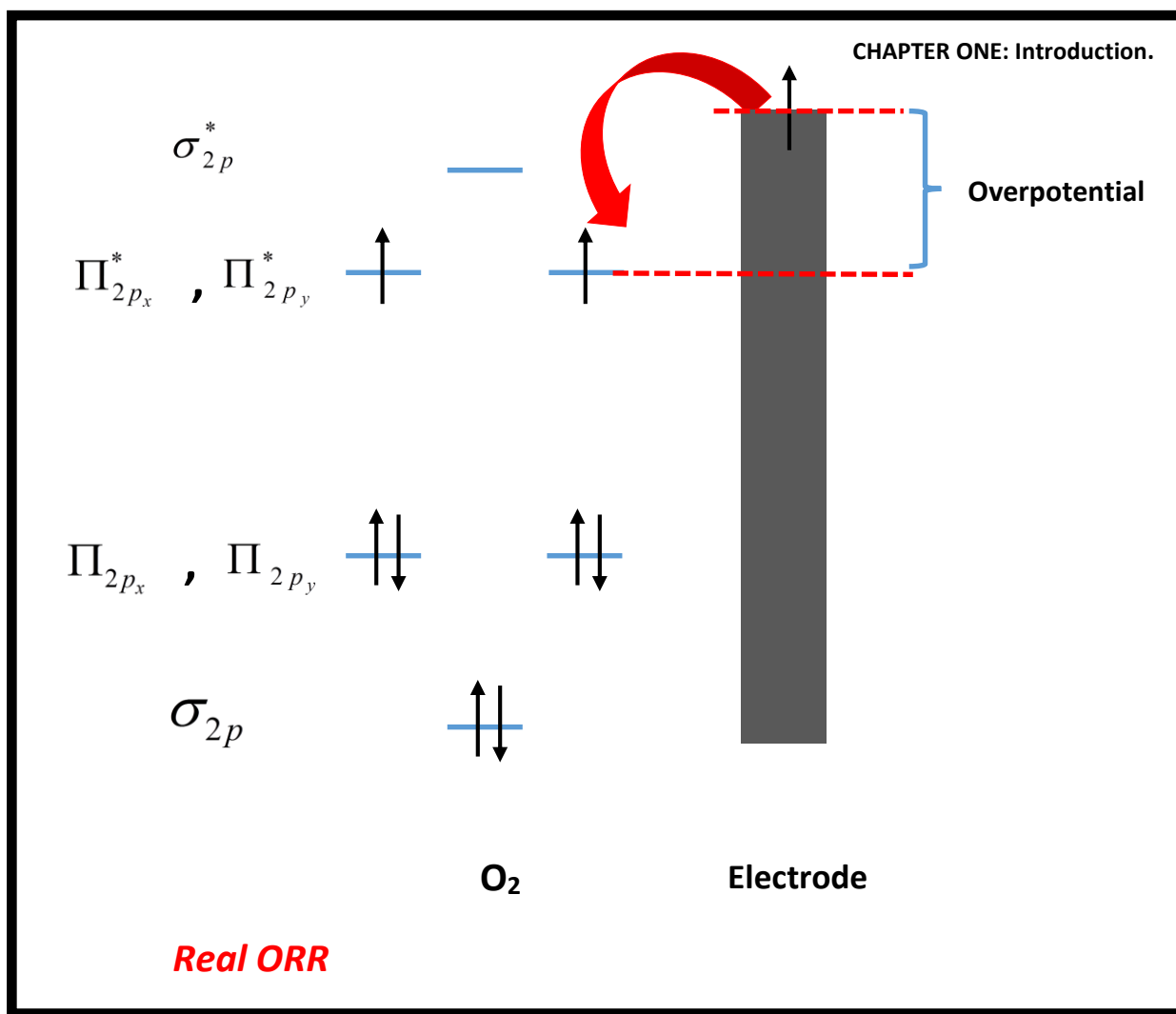


Fig. 1.14. A schematic representation of energy levels for real ORR.

ORR kinetics involves two main pathways i.e. a direct four electron reduction or a four electron via 2 electron intermediate and these processes depend on the pH of the redox media. The reactions are summarised in Table 1.4. Catalysts which can promote the four electron pathways are of great interest for the development of efficient fuel cells. It is demonstrated in this work that the nanocomposites have great potential for promoting a four electron ORR pathway.

Table 1.4. A summary of ORR pathways in acidic and alkaline conditions.

Electrolyte	ORR
Acidic aqueous solution	(i) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (ii) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
Alkaline aqueous solution	(i) $O_2 + H_2O + 4e^- \rightarrow 4OH^-$ (ii) $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ $OH_2^- + H_2O + 2e^- \rightarrow 3OH^-$

1.5. Scanning electrochemical microscopy (SECM).

The following is a list of the electrochemical techniques which were used for the characterisation of the electrocatalysts; cyclic voltammetry (CV), square wave voltammetry (SWV), rotating disk electrode (RDE) voltammetry, chronoamperometry (CA), electrochemical impedance spectroscopy (EIS), and scanning electrochemical microscopy (SECM). However, only SECM is given special attention in this section since it is less common. A brief explanation of other techniques is given at relevant sections of this thesis.

SECM is a technique used to characterize processes and structural features at the substrate using the current that flows through a very small electrode tip moving near

a conductive, semiconductive, or insulating substrate immersed in solution. The term SECM is used interchangeably for the technique and the instrument. The electrode tip can be moved normal to the substrate surface (i.e. z-direction) to probe the diffusion layer. A plot of tip current against tip-substrate distance gives an approach curve. In SECM the redox processes at the tip and substrate carry the current, and the electron transfer kinetics at the interface and mass transfer processes in solution determine the amount of current generated, hence the electrochemical activity at the substrate surface.

There are different modes of SECM experiments for probing activity at the tip or substrate i.e. (i) feedback mode, (ii) tip generation/tip collection (TG/SC) mode, (iii) substrate generation/tip collection (SG/TC), (iv) penetration mode, and (v) ion transfer mode [134,135]. The feedback mode has been used in this work. The feedback mode operates in either the negative or positive mode. The positive mode is shown in Fig. 1.15A in which the ultra-microelectrode (UME) approaches a conducting surface. When the tip-substrate distance is large (in the bulk solution) tip current is mainly due to mass transfer and the current observed is the limiting current (i_L). However towards the conducting substrate, faradaic currents increase (positive feedback). This results in the increase in tip currents illustrated in Fig. 1.15B. Conversely, when the tip approaches a non-conducting surface Fig. 1.16A, tip currents decrease due to hindered diffusion of the redox species to the UME tip.

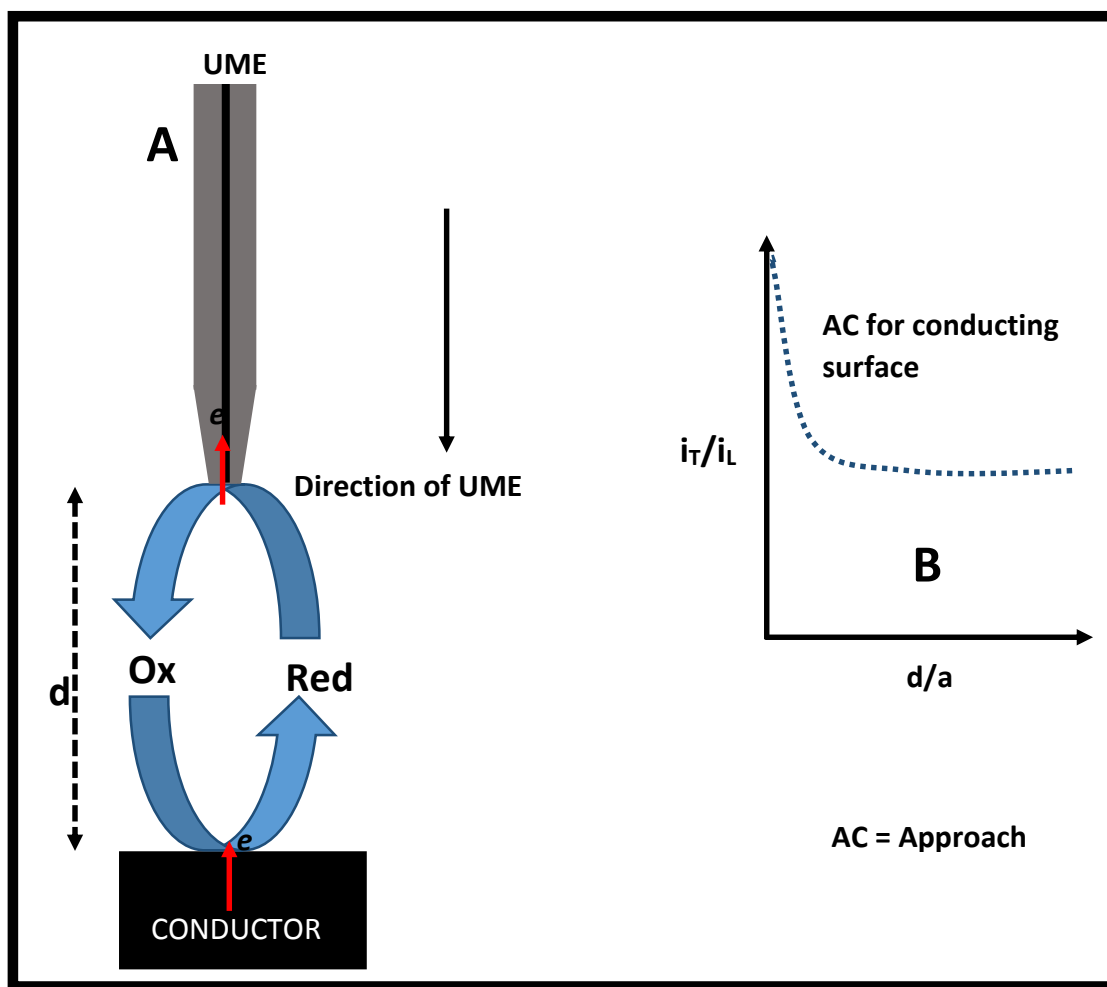


Fig. 1.15. UME moving towards a conducting substrate in a redox medium (A) and the corresponding approach curve (B). d = Tip-substrate distance, a = UME tip radius

The result of this hindered diffusion behaviour is a decrease in tip currents as illustrated in Fig. 1.16B. The tip can also be scanned across the surface in the x-y direction. A plot of current against distance moved for a single scan gives a line scan plot, Fig. 1.17.

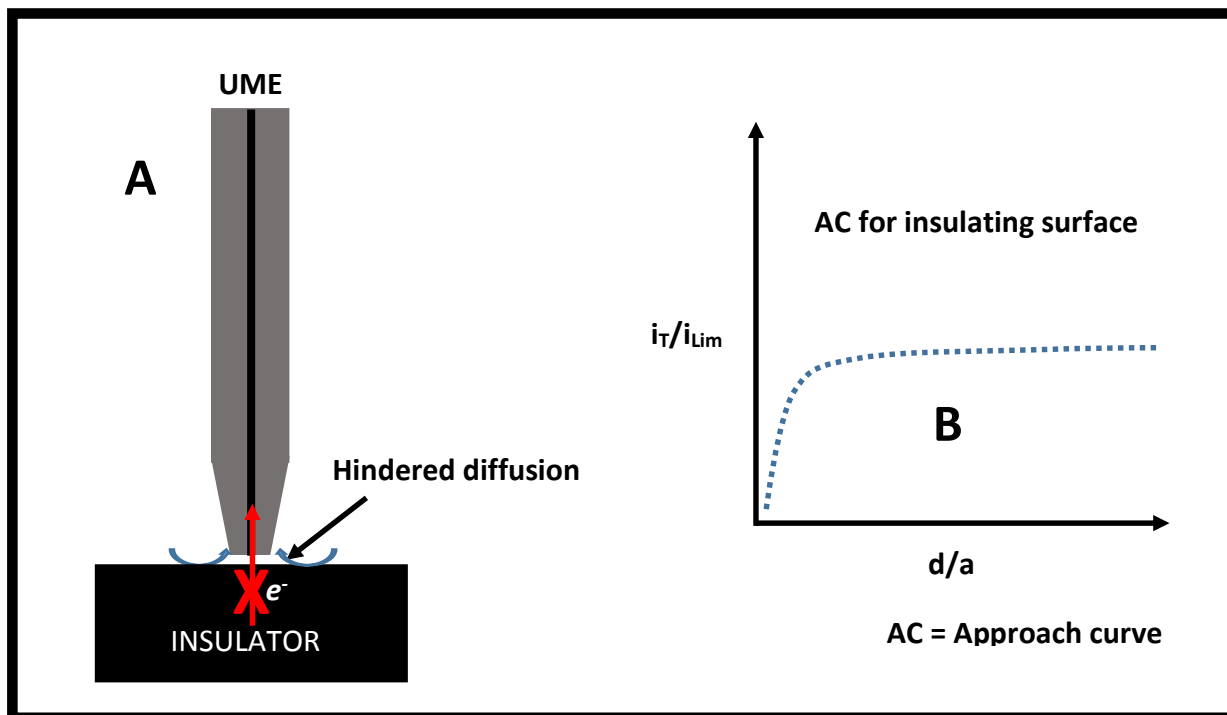


Fig. 1.16. UME moving towards a non-conducting substrate in a redox medium (A) and the corresponding approach curve (B).

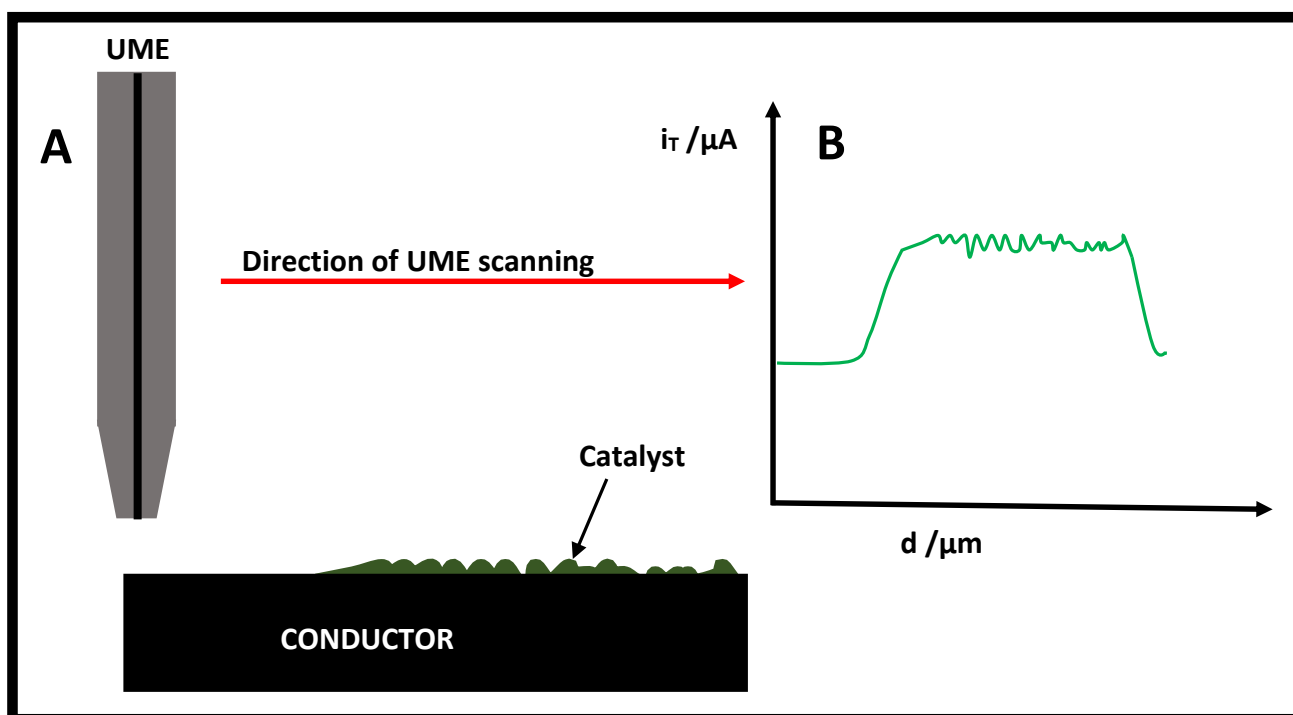


Fig. 1.17. UME moving across a substrate surface (x-y direction) in a redox medium (A) and the corresponding line scan (B).

Repetitive scanning in the x-y-direction gives an SECM image for a particular scan area, Fig. 1.18.

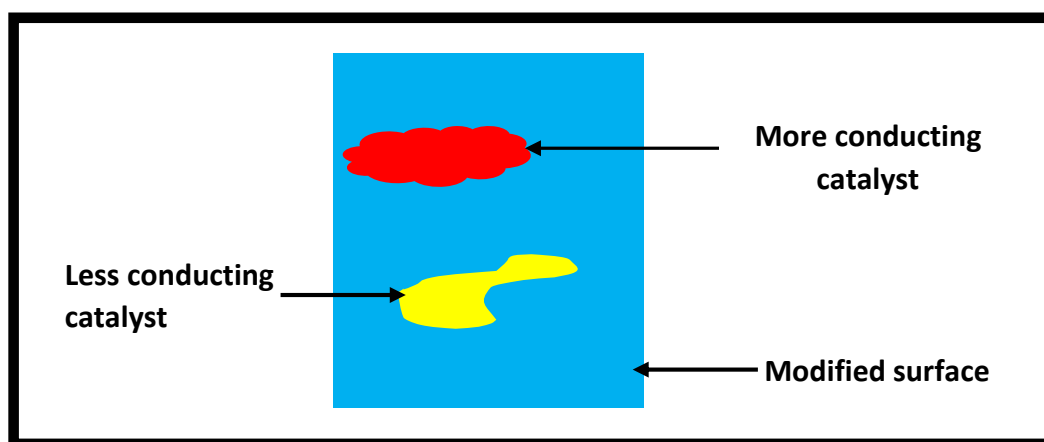


Fig. 1.18. An illustration of the appearance of a 2D SECM image of a substrate surface modified with two different catalysts.

Thus, the feedback mode experiments are used to probe into electrochemical reactivity of some of the prepared electrocatalysts, as well as electrochemically visualise their topography from SECM images.

1.6. Summary of aims of thesis

The focus of this work is on the enhancement of the electrocatalytic behaviour of MPCs using carbon nanomaterials in ORR, thiols oxidation and herbicide detection through;

- (a) Synthesis of new MPC containing bulkier substituents to reduce aggregation and electron donating groups for enhancement of electrocatalysis.

- (b) Using selected spacers/ intercalating agents (CdSe QDs and MWCNTs) to prevent agglomeration or restacking of graphene nanosheets during electrode modification for electrocatalysis.
- (c) Integration of poly-MPCs into a nanocomposite with MWCNT for electrocatalysis.
- (d) Iodine doping MPCs to improve electrocatalytic activity of nanocomposite catalysts for ORR.
- (e) Comparative analysis of the electrocatalytic behaviour of nanocomposites prepared through the sequential drop-dry against the premixing drop-dry method.
- (f) Comparative analysis of the electrocatalytic behaviour of MWCNTs covalently linked to CoPyPc, and when CoPyPc is adsorbed onto MWCNTs without a chemical bond.
- (g) Seeking non-precious ORR electrocatalysts which are highly electroactive and/or resistant to crossover effects with good electron transfer properties for the development of alternative cheap fuel cell prototypes showing very minimum overpotential.
- (h) Investigating the kinetics occurring at nanocomposite catalyst/electrolyte interface.

Chapter Two: Materials and Experimental.

2. Experimental.

2.1. Materials.

L-Cysteine, aluminium oxide, bulky MWCNTs, graphene oxide nanosheets (GONS), NaBH_4 , polycrystalline diamond suspensions (3F μm , 1F μm , and 0.25 μm), hexanol, hexane, acetone, absolute ethanol, cobalt chloride, CoPc, dicyclohexylcarbodiimide (DCC), 1, 8-diazabicyclo [5.4.0] undec-7-ene (DBU), tetrabutylammonium tetrafluoroborate (TBABF_4), paraquat, amitrole, diuron, urea and atrazine were obtained from Sigma-Aldrich. pH 4 buffer tablets were from Saarchem, 98% H_2SO_4 was obtained from B & M Scientific, 55% HNO_3 was obtained from Associated Chemical Enterprises, N,N-dimethylformamide (DMF) was obtained from Merck, Germany and was distilled before use. Aqueous solutions of l-cysteine and paraquat in pH 4 buffer were prepared using millipore water from Milli-Q Water Systems (Millipore Corp. Bedford, MA, USA). CoTAPc and complex 1, Scheme 3.1, were synthesized according to reported methods [136, 137].

2.2. Equipment.

- A Princeton Applied Research potentiostat/galvanostat Model 263A was used for all cyclic voltammetry (CV) and chronoamperometry (CA) studies. A three electrode electrochemical cell comprising of a glassy carbon electrode (GCE, geometric area = 0.071 cm^2) as the working electrode, $\text{Ag}|\text{AgCl}$ (3 M KCl) as reference electrode, and a platinum wire as the counter electrode was employed.

- Electrochemical impedance spectroscopy (EIS) studies were performed using an Autolab Potentiostat PGSTAT30 equipped with GPES software version 4.9. Electrochemical Impedance spectroscopy (EIS) studies were performed between 0.1 Hz and 10 kHz, using a 5 mV rms sinusoidal modulation, using an Autolab Potentiostat PGSTAT30 equipped with GPES software version 4.9. A nonlinear least squares (NNLS) method based on the EQUIVCRT programme was used for automatic fitting of the obtained EIS data.
- BAS100B electrochemical analyzer was used for the rotating disk electrode (RDE) studies.
- Scanning electrochemical microscopy (SECM) experiments were carried out with the Uniscan Instruments SCV 370, employing a three electrode cell with platinum SECM micro-tip, a platinum wire counter electrode, and a Ag|AgCl wire reference electrode. The approach curves and images were obtained using 25 μm and 15 μm diameter SECM tips, respectively. 2D and 3D SECM images were obtained from the raw data using SigmaPlot.
- Scanning electron microscopy (SEM) images were obtained using a TESCAN Vega TS 5136LM Electron microscope.
- Transmission electron microscope (TEM) micrographs for the nanoparticles and their conjugates were obtained using a Zeiss Libra 120 TEM operating at 80 kV.
- X-ray photoelectron spectroscopy (XPS) was done with a Kratos Axis UltraDLD, using an Al (monochromatic) anode, equipped with charge neutralizer and the operating pressure kept below 5×10^{-9} torr. For wide/survey XPS scans, the following parameters were used: emission current was kept at 5 mA and the Al anode voltage at 15 kV. The resolution used to acquire wide/survey scans

was at 160 eV pass energy using a hybrid lens in the slot mode. The centre used for the scans was at 520 eV and the width at 1205 eV, with steps at 1 eV and dwell times at 300 ms. For the high resolution scans, the resolution was changed to 40 eV pass energy in the slot mode. Curve fitting was performed using a Gaussian-Lorentzian peak shape after performing a linear background correction.

- Ground state electronic absorption spectra were performed on a Shimadzu UV-2550 spectrophotometer.
- Infrared spectra were recorded on Perkin Elmer 100 ART FT-IR spectrometer.
- Raman spectra were obtained using a Bruker Vertex 70-Ram II Raman spectrometer (equipped with a 1064 nm Nd: YAG laser and liquid nitrogen cooled germanium detector).
- Mass spectra data were collected with a Bruker Auto-FLEX III Smart beam TOF/TOF Mass spectrometer. The instrument was operated in positive ion mode using a m/z range of 400-3000 amu. The spectra were acquired using alpha-cyano-4-hydroxycinnamic acid as the MALDI matrix, using a 354 nm nitrogen laser.
- The elemental micro analysis was measured using Vario MICRO cube.
- Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EPR 300E X-band (10 GHz) spectrometer equipped with a TM probe with a flat quartz cell. The spin Hamiltonian parameters were obtained by simulation of the spectra. The static field (3400 G), center field (3500 G), modulation amplitude (19.19 G), time constant (10.24 ms), conversion time (5.12 msec), resolution (2048 pts), power (2.0×10^{-1} mW), and modulation frequency (100 kHz) were used as the experimental parameters at 298 K.

2.3. Synthesis of Pcs.

2.3.1. Synthesis of tetra(4-(4,6-diaminopyrimidin-2-ylthio)phthalocyaninatocobalt (II) (CoPyPc), Scheme 3.1.

A mixture of complex **1** (1.22 g, 4.55 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.23 g, 0.96 mmol) and DBU (0.5 mL, 3.35 mmol) was refluxed in hexanol under argon for 6 h. The reaction mixture was cooled down to room temperature and precipitated by adding methanol. After separation the product was washed with methanol and acetone through centrifuging until the solvent was clear, and allowed to dry. The dry product was further purified through Soxhlet extraction using methanol/water solvent mixture (1 :1 by volume) for 24 h to give CoPyPc.

Yield: (0.43 g, 45.37%) IR (KBR, cm^{-1}): 3331, 1600 (NH) 1579 (C=C) 2928, 1455 (C-H). UV-Vis (DMF): λ_{max} nm (log ϵ), 675 (4.5), 620 (4.1). MS (m/z): Calculated 1135 g/mol Found: 1131 (M+4 H). Calculated for $\text{C}_{48}\text{H}_{35}\text{CoN}_{24}\text{S}_4$: C 50.7, H 3.1, N 29.6; Found C 49.90, H 3.5, N 29.20.

2.3.2. Preparation of iodine doped CoPyPc.

The finely ground CoPyPc (38.4 mg, 0.03 mmol) was added into a closed container containing 8 ml of iodine saturated dichlorobenzene solution and stirred for 48 h. The iodine doped CoPyPc collected by centrifugation, washed with several portions of hexane until the solvent remained colourless, and dried in an oven at 70 °C. The final product is designated iodine doped-CoPyPc from here onwards.

UV-vis (DMF): λ / nm (log ϵ) nm, 676 (5.1), 609 (4.0), Calculated MW for undoped CoPyPc (1135 g/mol). Calc (using 3 iodines as found by elemental) for doped CoPyPc:

1515.7, found: 1261.7 [M -2I⁻]. Anal. Calc. for doped C₄₈H₃₅CoN₂₄S₄I₃: C 38.00, H 2.30, N 22.17; Found C 37.91, H 2.89, N 20.7.

2.4. Preparation of nanomaterials.

2.4.1. Preparation of reduced Graphene nanosheets (rGNS), Scheme 3.2.

Graphene oxide nanosheets (0.1 g) were dispersed in 100 ml Milli pore water through ultrasonication. NaBH₄ (0.57 g, 15 mmol) was added to reduce the graphene oxide sheets, followed by heating at 70 °C for 3 h. The black solid product obtained by filtration over a fritted glass funnel, was washed with copious amount of water (5 x 50 ml), and dried in an oven at 70°C. The resulting sample is designated rGNS-1. A portion of rGNS-1 was further treated with 98% H₂SO₄ and the product was collected and designated rGNS-2. The H₂SO₄ was employed to eliminate the aliphatic functionality and dehydrate the remaining hydroxyl functionalities to form alkenes that resemble graphitic sp² carbon network [138].

2.4.2. Preparation of carboxylic acid functionalized MWCNT (MWCNT-COOH), Scheme 3.3 (Compound II).

The functionalization of MWCNT was achieved through a less vigorous and established procedure [139], however with slight alterations. Briefly, MWCNT (400 mg) were dispersed in 20 mL of 55 % HNO₃, and refluxed between 55 °C- 60 °C for 2 hrs. The resulting suspension was allowed to cool to room temperature and 20 mL of Milli pore water were added to reduce the acidity. The suspension was centrifuged and washed with Millipore water several times until a pH of 5.27 was achieved. The functionalised MWCNT were dried in an oven at 60 °C for 24 h.

2.4.3. Preparation of MWCNT intercalated reduced graphene nanosheets.

A mixture of rGNS-2 and MWCNT (9:1 by mass) was added to 200 mL millipore water and sonicated for 5 h to obtain the rGNS-2 and MWCNT suspension. The solid was filtered and washed several times with Millipore water, absolute ethanol, and dried in an oven at 70 °C. The resulting sample is designated rGNS-2-MWCNT in this work.

2.4.4. Preparation of covalently linked MWCNT-COOH and CoPyPc (MWCNT-CoPyPc), Scheme 3.3 (Compound III).

The CoPc derivatives were covalently linked to MWCNT-COOH through conversion of the carboxylic acid functional groups of MWCNT to active carbodiimide ester groups [140]. Briefly, MWCNT-COOH (100 mg) were ultrasonicated in 15 mL DMF until an intense black suspension was obtained. The black suspension was centrifuged at 3200 rpm for 10 min to afford a black and homogeneous supernatant solution. The solution was collected in a vial and stirred with DCC (50 mg, 0.24 mmol) for 48 h at room temperature. CoPyPc (100 mg, 0.088 mmol) was added and stirring continued for another 48 h. The crude product was washed several times with ethanol through centrifuging to remove excess DCC, DMF, and free CoPyPc. Washing was repeated until the solvent could not turn green after centrifuging. The nanocomposite was oven dried at 60 °C for 48 h.

2.4.5. Preparation of non-covalently linked MWCNT-COOH and CoPyPc (MWCNT/CoPyPc), Scheme 3.3, Compound (IV).

Immobilization of CoPyPc onto MWCNT-COOH was achieved following established procedures [141], however with minor alterations. In brief, MWCNT-COOH (50 mg) were dispersed in 10 mL dry DMF through ultrasonication for 15 min to afford a homogeneous suspension. CoPyPc (50 mg, 0.044 mmol) was added and a green

suspension obtained. The resulting mixture was stirred for 72 h, followed by precipitation using ethanol, and the solid product obtained by centrifugation. Centrifugation was repeated several times until the solvent was clear to ensure complete removal of unadsorbed CoPyPc.

2.5. Electrode modification.

For all electrode modifications, the glassy carbon working electrode surface was polished using silicon carbide grinding paper (grit 1200) followed by polishing on a Buehler-felt pad using alumina ($<10\ \mu\text{m}$). Between each polishing step, brief sonication in absolute ethanol was used to remove any impurity. After sonication the electrode was polished again using alumina, then rinsed with Millipore water and dried under argon. With the exception of ORR, all solutions were purged with argon gas for 15 min to drive out oxygen before each cyclic voltammetry analysis, and the atmosphere of argon was maintained throughout the period of analysis.

2.5.1. CoTAPc based electrodes.

2.5.1.1. MWCNT-CoTAPc.

CoTAPc (1 mM) and the MWCNTs (0.5 mg/mL) were separately dissolved in distilled DMF and the later was dispersed through ultrasonication for 5 min. The GCE was modified by the drop-dry method using the following procedures;

(a) Premixed drop-drying

A drop of the 1 mM CoTAPc mixed with a drop of 0.5 mg/mL MWCNTs was placed on the GCE and allowed to dry {represented as CoTAPc-MWCNT (premixed)}.

(b) Sequential drop-drying

A drop of 0.5 mg/mL MWCNTs was allowed to dry on GCE, followed by a drop of 1 mM CoTAPc {represented as CoTAPc-MWCNT (sequential)}. Experiments were also performed where CoTAPc was employed in the absence of MWCNTs. Furthermore, experiments were also performed with CoTAPc adsorbed first, followed by MWCNT but there was insignificant catalytic activity, hence are left out of the discussion.

2.5.1.2. rGNS-MWCNT-CoTAPc (sequential).

In order to check the effect of nanomaterials alone (without CoTAPc), GONS, rGNS-1, rGNS-2 or rGNS-2-MWCNT were also used to modify GCE. rGNS-1-MWCNT was not explored further since rGNS-1 was found to be inferior relative to rGNS-2. For CV, SWV and SECM studies, a 10 mg sample of each of GONS, rGNS-1, rGNS-2 or rGNS-2-MWCNT was separately added to 1 mL of DMF and then subjected to ultrasonication for 10 h to promote even dispersion. The suspensions (5 μ L) of each were placed on GCE surface and dried. The resulting electrodes are designated as GONS-GCE, rGNS-1-GCE, rGNS-2-GCE or rGNS-2-MWCNT-GCE. For the preparation of rGNS-2-MWCNT-CoTAPc-GCE (sequential), 1 mg CoTAPc was dissolved in 1 mL DMF and a drop (5 μ L) of it was added on top of rGNS-MWCNT layer followed by drying. The mass ratio of the rGNS-2-MWCNT to CoTAPc was a 10:1. Experiments where CoTAPc alone (represented as CoTAPc-GCE) and where individual nanomaterials were used in the presence of CoTAPc were also performed for comparative purposes i.e. CoTAPc drop-dried on MWCNT (represented as CoTAPc-MWCNT-GCE) and CoTAPc drop-dried

on rGNS-2 (represented as CoTAPc-rGNS-2-GCE). The nanocomposites were sequentially prepared.

2.5.1.3. Polymerization of CoTAPc.

Poly-CoTAPc-GCE was prepared by repetitive cyclic voltammetry scanning of the bare GCE in 1×10^{-3} M CoTAPc solution prepared in DMF containing 0.1 M TBABF₄ electrolyte. Poly-CoTAPc-MWCNT-GCE was prepared in two stages; (i) 0.5 μ L MWCNT (1 mg per 1 mL DMF) was drop-dried onto the GCE, followed by (ii) repetitive cyclic voltammetry scanning of the MWCNT modified GCE in 1.0×10^{-3} M CoTAPc solution. After the end of each repetitive scanning process, the electrode was rinsed with dry DMF and dried under argon before each use.

2.5.2. CoPyPc based electrodes.

Polymerization of CoPyPc was just as stated for CoTAPc in section 2.5.1.3.

2.5.2.1. rGNS-2-CdSe-QDs-CoPyPc.

rGNS-2, CdSe-QDs and CoPyPc (1 mg each, corresponding to 0.88 mmol for CoPyPc) were added separately to 10 mL DMF. First rGNS-2 and CdSe-QDs suspensions (1 mL each) were mixed and sonicated to allow deposition of CdSe-QDs on reduced graphene nanosheets, following literature methods [142]. The resulting suspension is designated rGNS-2-CdSe-QDs. rGNS-2-CdSe-QDs (1 μ L) was deposited on a polished GCE, dried in an oven at 60 °C. CoPyPc (1 μ L) was added on top of the dried rGNS-2-CdSe-QDs, and dried again in an oven at 60 °C. The resulting nanocomposite is designated CoPyPc-rGNS-2-CdSe-QDs (sequential). Electrodes where CoPyPc, r-GNS-2 and CdSe-QDs (1 mL of 1 mg solution in DMF was employed for each) were

individually deposited on to the GCE followed by addition of CoPyPc (1 mL of 1 mg solution in DMF) for the latter two, were also employed.

2.5.2.2. Iodine doped CoPyPc based electrodes.

The GCE was modified with iodine doped-CoPyPc and iodine doped-CoPyPc-MWCNT through adsorption from DMF solutions. To prepare the nanomaterials solutions/suspensions, 1 mg each of iodine doped-CoPyPc and MWCNT (used as received) was dissolved in 2 mL DMF, and sonicated to give a homogeneous solution/suspension. Further dilution of each solution was done by taking 1 mL and dissolving it in 10 mL DMF. From the diluted solutions, 1 μ L of each was allowed to dry on GCE surface (sequential). For the modification of the GCE with iodine doped-CoPyPc-MWCNT, 1 μ L MWCNTs was allowed to dry on GCE, followed by addition of 1 μ L iodine doped-CoPyPc. CoPc was also used for comparison. The preparation of CoPc was as described for iodine doped-CoPyPc above.

Publications

The work presented in this thesis has been published or submitted to the following peer reviewed journals:

1. **Stephen Nyoni**, Philani Mashazi, Tebello Nyokong, Electrocatalytic behaviour of nanocomposites of electropolymerised cobalt phthalocyanines supported on multi-walled carbon nanotubes modified glassy carbon electrode, 2015, *J. Solid State Electrochemistry* (accepted and in press).
2. **Stephen Nyoni**, Tebello Nyokong, Comparative electrocatalytic studies of nanocomposites of mixed and covalently linked multiwalled carbon nanotubes and 4-(4,6-diaminopyrimidin-2-ylthio) phthalocyaninatocobalt(II), *Polyhedron*, 98, 2015, 47-54.
3. **Stephen Nyoni**, Philani Mashazi, Tebello Nyokong, Iodine-doped Cobalt Phthalocyanine supported on Multi-walled Carbon Nanotubes for Oxygen Reduction Reaction, *Electroanalysis*, 27, 2015, 1156-1187.
4. **Stephen Nyoni**, Tebello Nyokong, Development of Graphene/CdSe Quantum Dots-Co Phthalocyanine Nanocomposite for Oxygen Reduction Reaction, *Electroanalysis*, 26, 2014, 2261 - 2272.
5. **Stephen Nyoni**, Tebello Nyokong, Electrocatalytic behaviour of cobalt phthalocyanine in the presence of reduced graphene nanosheets and of multi-walled carbon nanotubes, *Electrochimica Acta*, 136, 2014, 240-249.
6. **Stephen Nyoni**, Tawanda Mugadza, Tebello Nyokong, Improved L-cysteine electrocatalysis through a sequential drop-dry technique using multi-

Publications

walled carbon nanotubes and cobalt tetraamino phthalocyanine conjugates, *Electrochimica Acta*, 128, 2014, 32-40.

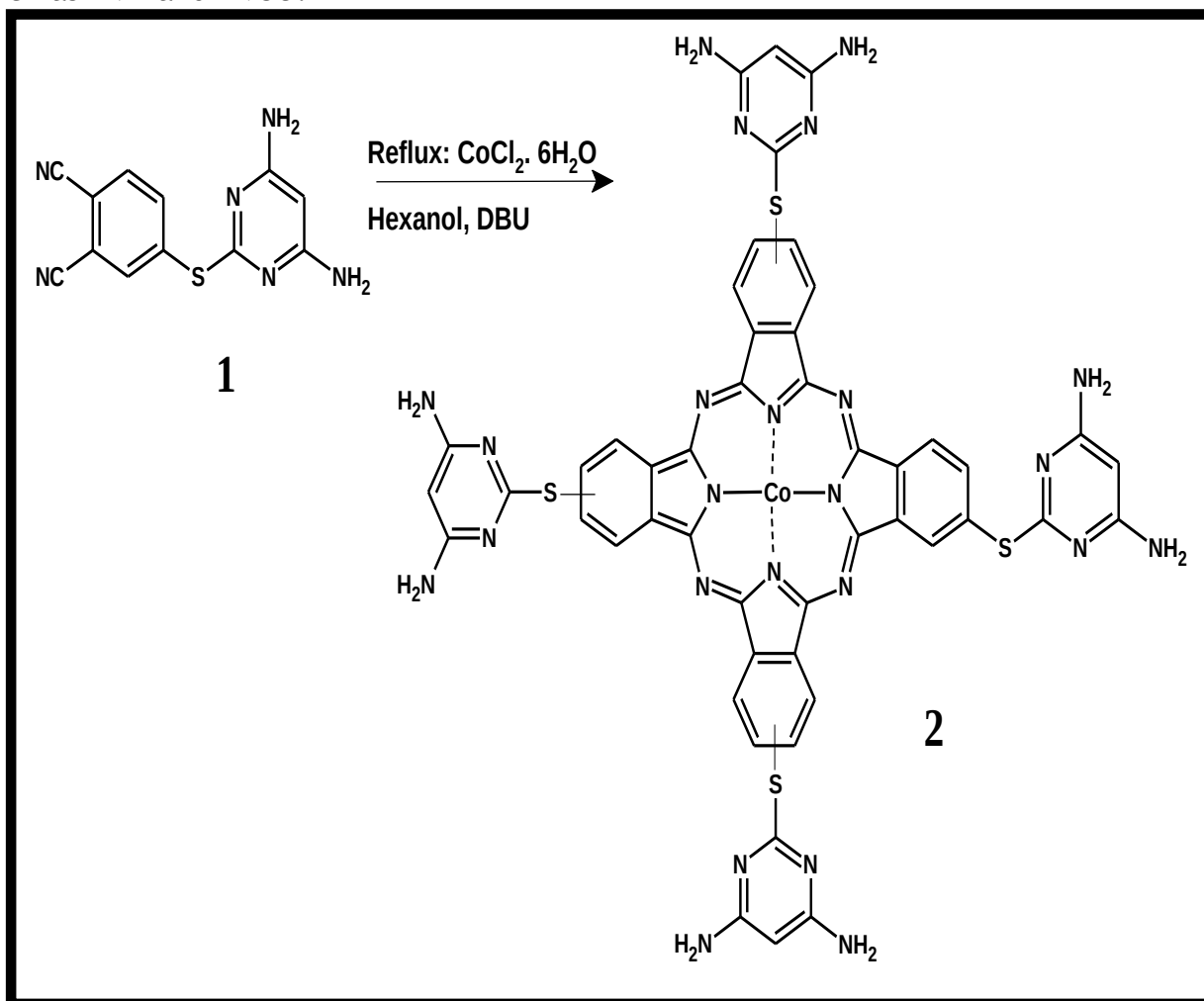
Chapter Three: Characterisation.

This chapter deals with characterization of Pcs nanomaterials and their nanocomposite electrocatalysts.

3.1. Characterization of CoPyPc and its iodine doped form.

3.1.1. CoPyPc.

The pathway for the synthesis of CoPyPc (**2**) is shown in Scheme 3.1. There are four possible isomers, but they were not separated. Cyclotetramerization of compound **1** took place in the presence of cobalt chloride. Purification was accomplished by washing using water/methanol (1 : 1 by volume), this was followed by further purification using Soxhlet apparatus for 24 h. The complex was soluble in solvents such as DMF and DMSO.



Scheme 3.1. Scheme for the preparation of CoPyPc (**2**).

Characterization of the complex was carried out using IR and mass spectroscopies as well as elemental analysis. NMR data was not included due to the paramagnetic nature of the central metal. The results obtained were consistent with the predicted structures shown in Scheme 3.1. There is a clear disappearance of CN-stretch from the IR spectrum (Fig. 3.1A) of 4-(4,6-diaminopyrimidin-2-ylthio) phthalonitrile (2335 cm^{-1}) compared to CoPyPc (Fig. 3.1B) showing successful cyclization.

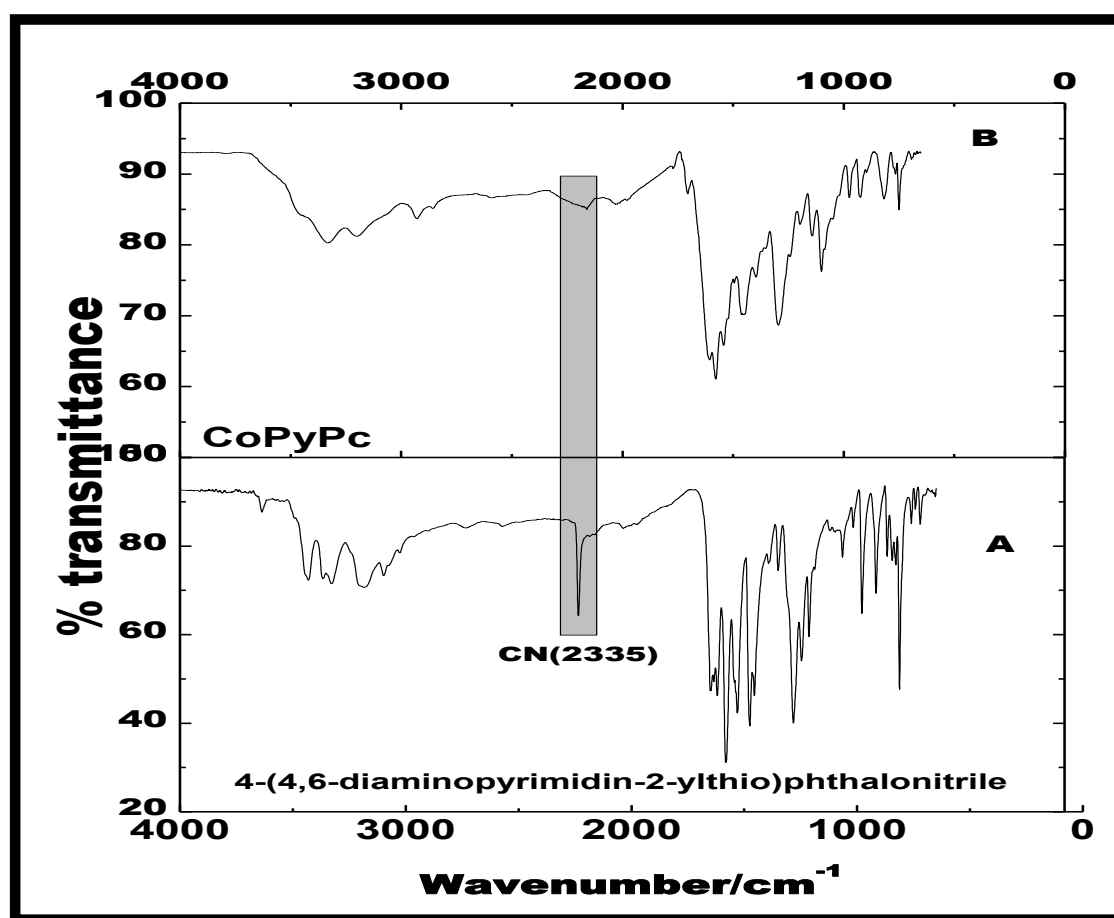


Fig. 3.1. IR spectra of (A) compound 1 and (B) CoPyPc (2).

3.1.2. Iodine Doped CoPyPc.

Characterization of the iodine-doped CoPyPc complex was carried out using mass spectroscopy as well as elemental analysis. Elemental data indicate the presence of three iodines doped on CoPyPc. Mass Spectrometry (MS) results show that there is only one iodine atom doped on CoPyPc. This might be attributable to loss of two iodines during the ionization process. Iodine doping of Pc complexes occurs by partially oxidizing the Pc accompanied by partially reduced iodines [143]. The FTIR spectra did not show any significant changes between the spectra of CoPyPc and iodine-doped CoPyPc. The lack of changes in the FTIR spectra has been observed for single walled carbon nanotubes (SWCNT) vibrations on iodine doping, except for changes in peak intensities [144,145].

3.1.2.1. UV-Vis Absorption Spectra.

Fig. 3.2 shows the UV-Vis spectra of CoPyPc and iodine doped-CoPyPc in DMF.

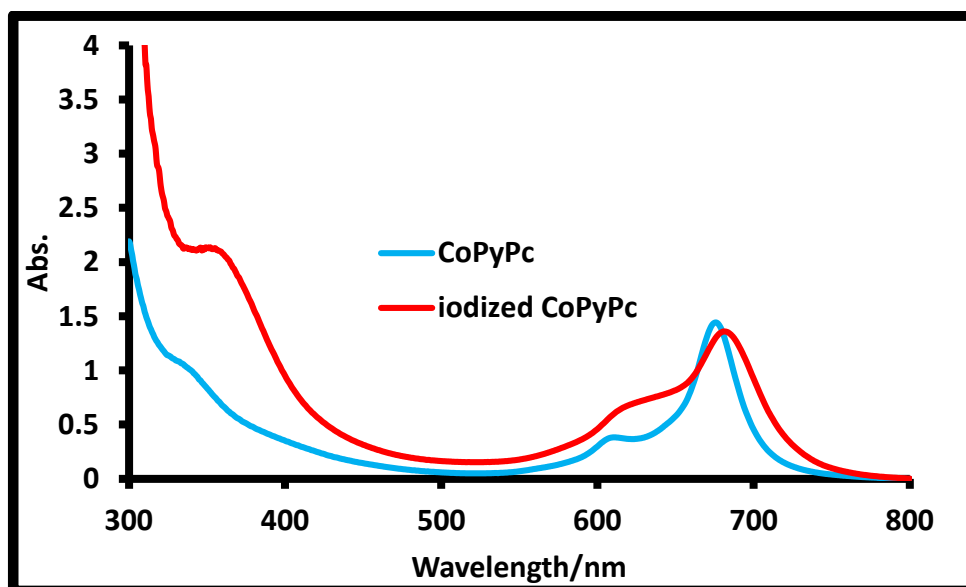


Fig. 3.2. UV-Vis spectra of CoPyPc and iodine doped-CoPyPc in DMF.

The Q-band (676 nm) is red-shifted for CoPyPc when compared to unsubstituted CoPc at (662 nm), Table 3.1, due to the presence of the electron donating amino and sulphur groups on the ring substituent, which are known to result in red shifting of the Q band [146]. After iodine doping there was more red-shifting of the Q-band from 676 nm of CoPyPc to 682 nm, Fig. 3.2.

Table 3.1: Spectral data of the nanocomposites.

Nanomaterials/ Nanocomposites	Absorption maxima (nm) in DMF
CdSe-QDs	568
rGNS-2	---a
CoPc	662
CoPyPc	676
Iodine doped CoPyPc	682
CoPyPc-MWCNTs (mixed)	682
CoPyPc-MWCNTs (linked)	680
CoPyPc-rGNS-2 (mixed)	682
rGNS-2-CdSe-QDs (mixed)	568
CoPyPc-CdSe-QDs (mixed)	680
CoPyPc-rGNS-2-CdSe-QDs (mixed)	672

a = no defined peaks.

The red shift of the Q-band in the spectra on iodine doping of phthalocyanine has been reported [109] suggesting the narrowing of the HOMO-LUMO energy gap. The spectrum of the iodine doped CoPyPc also shows broadening. The broadening of the Q band was attributed to the presence of a radical species [109].

3.1.2.2. Electron Paramagnetic Resonance (EPR).

The presence of a radical was clearly proved in this work using EPR, Fig. 3.3. The spectrum confirmed the presence of an unpaired electron in iodine doped CoPyPc ($g = 2.0044$), confirming the presence of organic radicals on the doped CoPyPc. There was a very poor signal from the undoped CoPyPc as shown in Fig. 3.3 Inset, implying the absence of radicals in this catalyst.

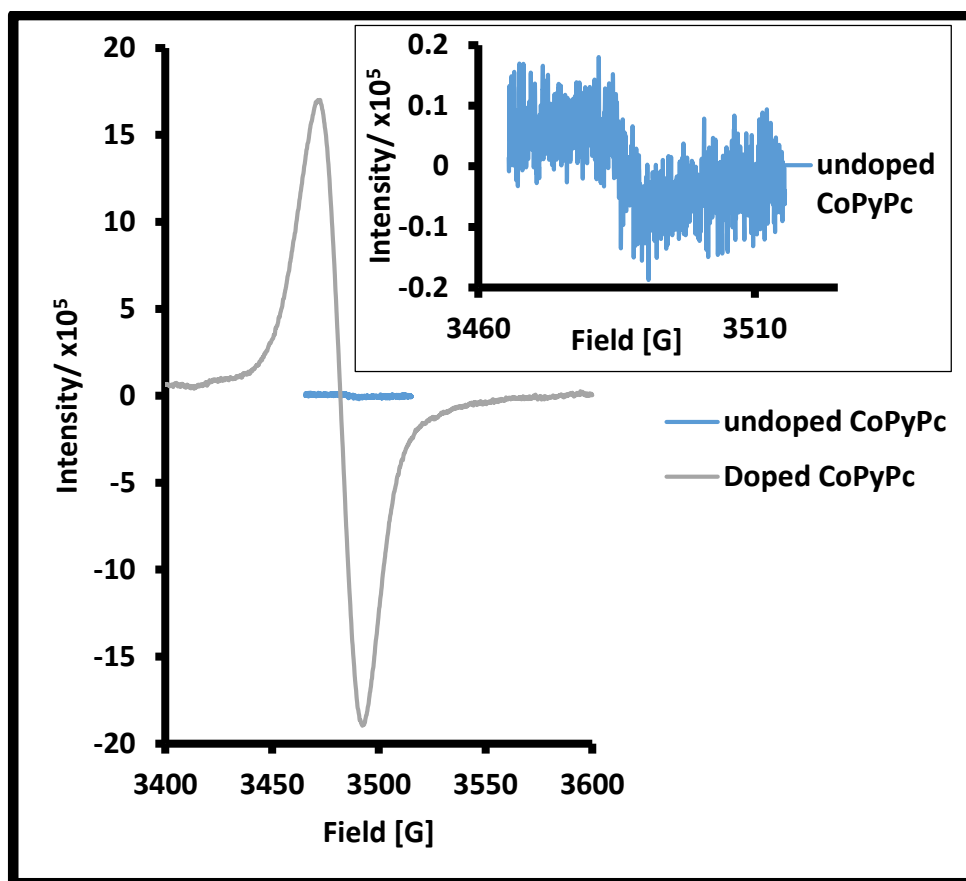
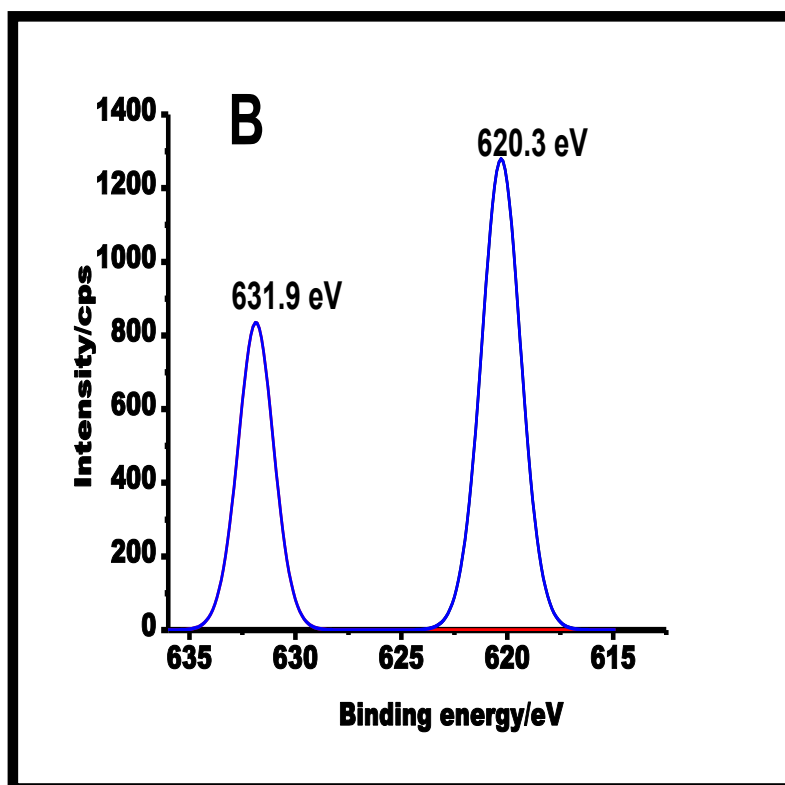
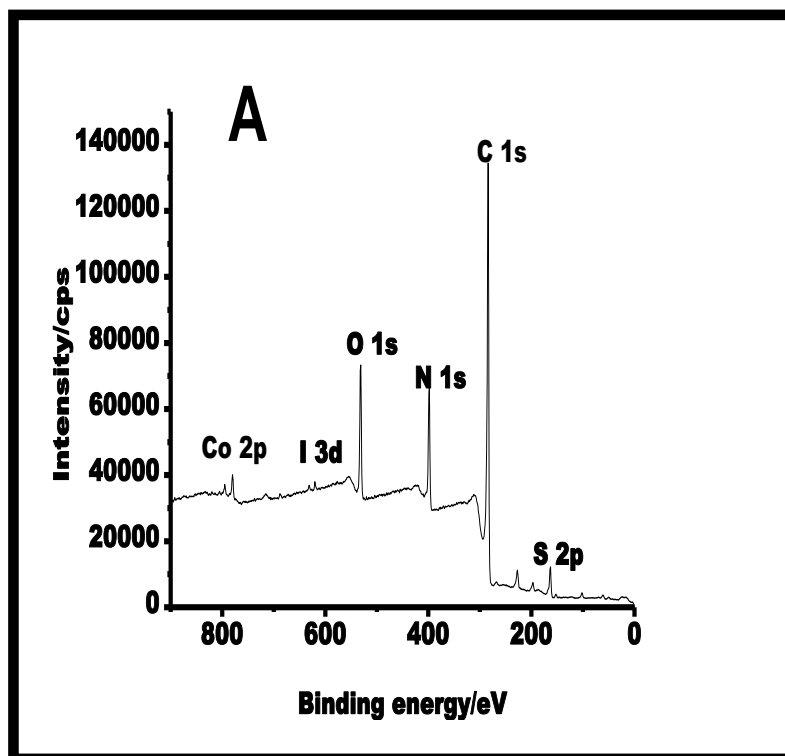


Fig. 3.3. EPR spectra of undoped CoPyPc and iodine doped CoPyPc. Insert = undoped CoPyPc when not overlaid.

3.1.2.3. X-ray Photoelectron Spectroscopy (XPS).

To probe into the presence of iodine species in the iodine-doped cobalt phthalocyanine, XPS measurements were carried out. The I 3d peak is seen from the XPS survey spectrum of the iodine-doped cobalt phthalocyanine in Fig. 3.4A (near 630 eV).



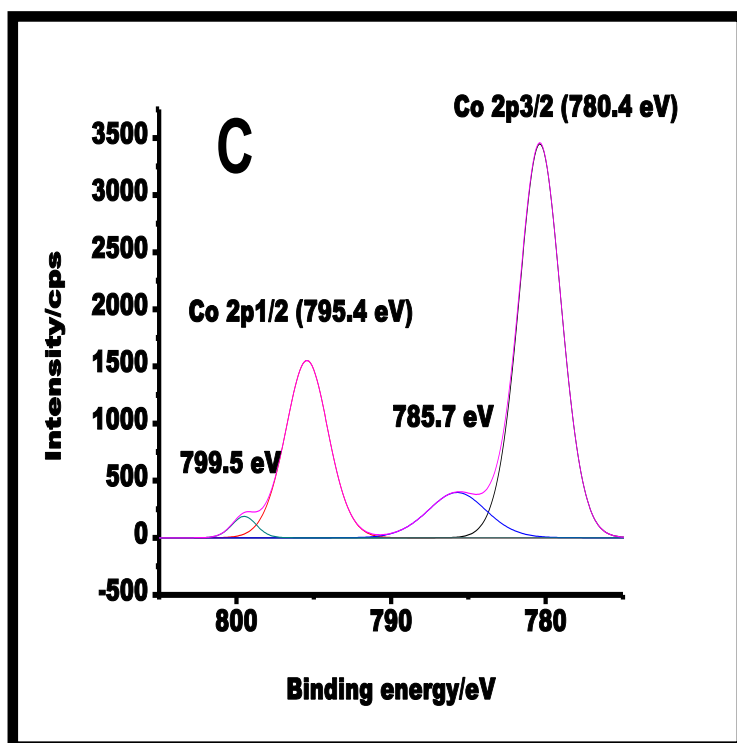


Fig. 3.4. XPS survey for iodine doped CoPyPc (A), XPS deconvoluted spectra for I 3d (B), and Co 2p (C).

It is interesting to note that an O 1s peak was also observed even though it was not expected from the structure of the iodine doped cobalt phthalocyanine. The presence of oxygen can be attributed to a strong physical adsorption of oxygen to the catalyst surface which continuously occurs from the time of modification until the sample is placed in the XPS vacuum chamber. It has been observed that oxygen saturated SWCNTs have higher electrical conductivity than SWCNT with less adsorbed oxygen [147]. This is a significant property for a material destined for ORR. The relative carbon to oxygen ratio was found to be 9 for the iodine doped cobalt phthalocyanine, whereas in the undoped cobalt phthalocyanine the ratio was 8, showing a slight improvement in the interaction of the catalyst with oxygen upon

doping. We suggest that the presence of radicals on the doped catalyst results in more chemisorbed triplet oxygen species.

The bond length for the chemisorbed O-O is relatively longer than physisorbed oxygen species, resulting in weak interaction between O-O, hence allowing strong interaction with adjacent carbon atoms of the catalyst [148]. Chemisorption is likely to give rise to a higher carbon to oxygen ratio observed from XPS, since such interaction would result in minimum oxygen desorption when the sample is placed in the ultra-high vacuum chamber for XPS analysis.

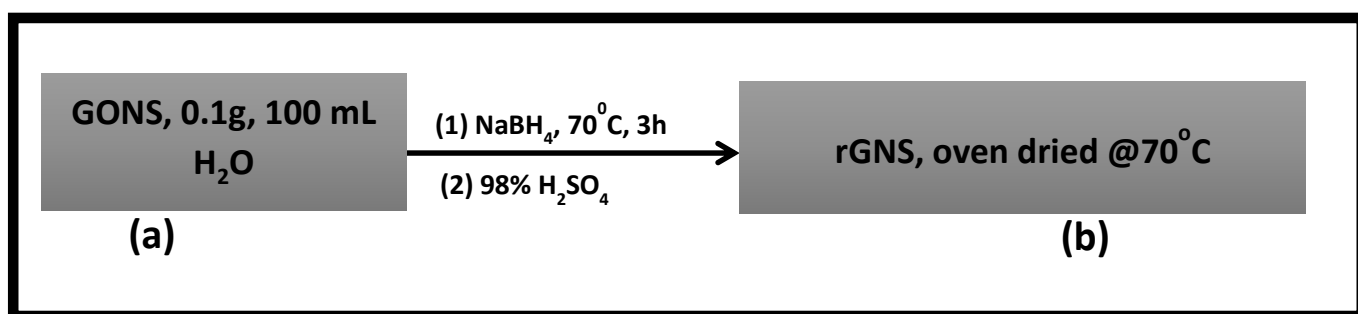
Fig. 3.4B shows the high resolution XPS I 3d spectrum with peaks at 620.3 eV and 631.9 eV with a peak separation of $\Delta = 11.6$ eV. The peak split corresponds to the spin orbit coupling of iodine 3d to I 3d_{3/2} (631.9 eV) and I 3d_{5/2} (620.3 eV). These binding energy values are consistent with covalently bound iodine atom since ionic iodine shows a peak at around 618.8 eV (3d_{5/2}) [149]. The absence of this peak from the electrocatalyst (figure not shown) implies that the CoPyPc/iodine interaction is mainly covalent, and unreacted KI was successfully removed from the final product through thorough rinsing.

Fig. 3.4C shows deconvoluted Co 2p XPS spectra. Two distinct peaks at 780.4 eV and 795.4 eV are assigned to Co 2p_{3/2} and Co 2p_{1/2}, respectively, for Co²⁺ within the phthalocyanine ring of CopyPc. The peaks observed at 785.7 eV (9.7% atomic concentration) and 799.5 eV (1.9% atomic concentration), are assigned to the satellite features for Co 2p_{3/2} and Co 2p_{1/2}, respectively. Satellite splitting (the

difference between Co 2p_{3/2} and its satellite peak depends on the oxidation state. For Co²⁺ the value has been reported to lie between 5 and 6 eV and for Co³⁺ the value is around 9 eV [150]. The separation between the Co 2p_{3/2} peak and its satellite was found to be 5.3 eV and this is consistent with the +2 oxidation state for Co [150]. Thus in this work, satellite splitting shows that the metal oxidation state remained as Co²⁺ even after doping.

3.2. Characterisation of graphene and its nanocomposites.

Reduction of GONS results in large changes in their microstructure and properties. Scheme 3.2 shows reduction of GONS to form rGNS and its nanocomposites. Reduction of GONS results in enhancement of the conjugation system and an increase in the C:O ratio. Consequently, electron transfer is promoted. Visual characteristics, Raman spectroscopy and XPS were important tools employed in this work to elucidate the extent of GONS reduction.



Scheme 3.2. Preparation of reduced Graphene Nanosheets (rGNS).

3.2.1. Visual characterisation.

A clear indication of reduction was the formation of a charcoal black suspension (of rGNS-2) from the original brilliant-brown suspension (of GONS) as shown in Fig. 3.5A. This behaviour is thought to emanate from an increase in the hydrophobicity of the rGNS due to a decrease in sheet surface polar functionalities [80]. The difference in the extent of reduction using NaBH_4 (rGNS-1) or NaBH_4 followed H_2SO_4 (rGNS-2) is shown by the resultant suspension i.e. a transparent brownish rGNS-1 suspension and a charcoal-black suspension for rGNS-2, Fig. 3.5A. NaBH_4 has moderate efficiency in removing oxygen functionalities relative to concentrated sulphuric acid (98%).

It has been reported that acid treatment dehydrates the remaining tertiary alcohols to form alkenes that adds to the sp^2 of the graphitic structure [138]. There was no observable colour change when MWCNT were added to rGNS-2, Fig. 3.5A. Furthermore, the increase in electrical conductivity due to improved charge carrier concentration and mobility enhances incident light reflection. This gives the rGNS their metallic lustrous appearance as shown in Fig. 3.5B.

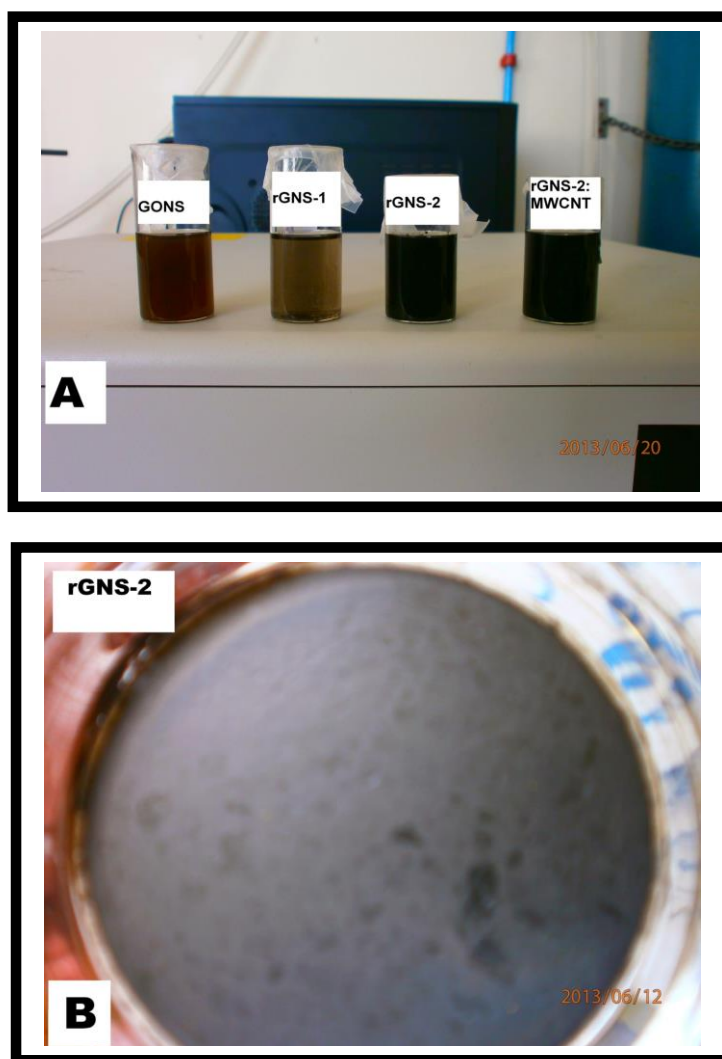


Fig. 3.5. Suspension of GONS and reduced graphenes in DMF (A). The lustrous appearances of reduced graphene nanosheets over a fritted glass funnel (B).

3.2.2. Raman Studies of reduced graphene nanosheets.

Carbon materials are known to show some characteristic Raman peaks which are centered around 1500 cm^{-1} (G, tangential mode; sp^2) and 1270 cm^{-1} (D, disorder band; sp^3) [151,152]. The D:G ($\text{sp}^3:\text{sp}^2$) ratio is generally considered as a quality parameter to determine the extent of functionalization of the carbon nanomaterials. This is

because the G-band is not affected by defects, whereas the D-band is enhanced by the presence of sp^3 defects in the sp^2 lattice [151]. D:G ratio gives information on establishment of sp^2 hybridization and deoxygenation. The D-band for rGNS-1 (0.00158) is more intense than that D-band for rGNS-2 (0.00136), Fig. 3.6. This shows that there are less sp^3 defects in the sp^2 lattice of rGNS-2.

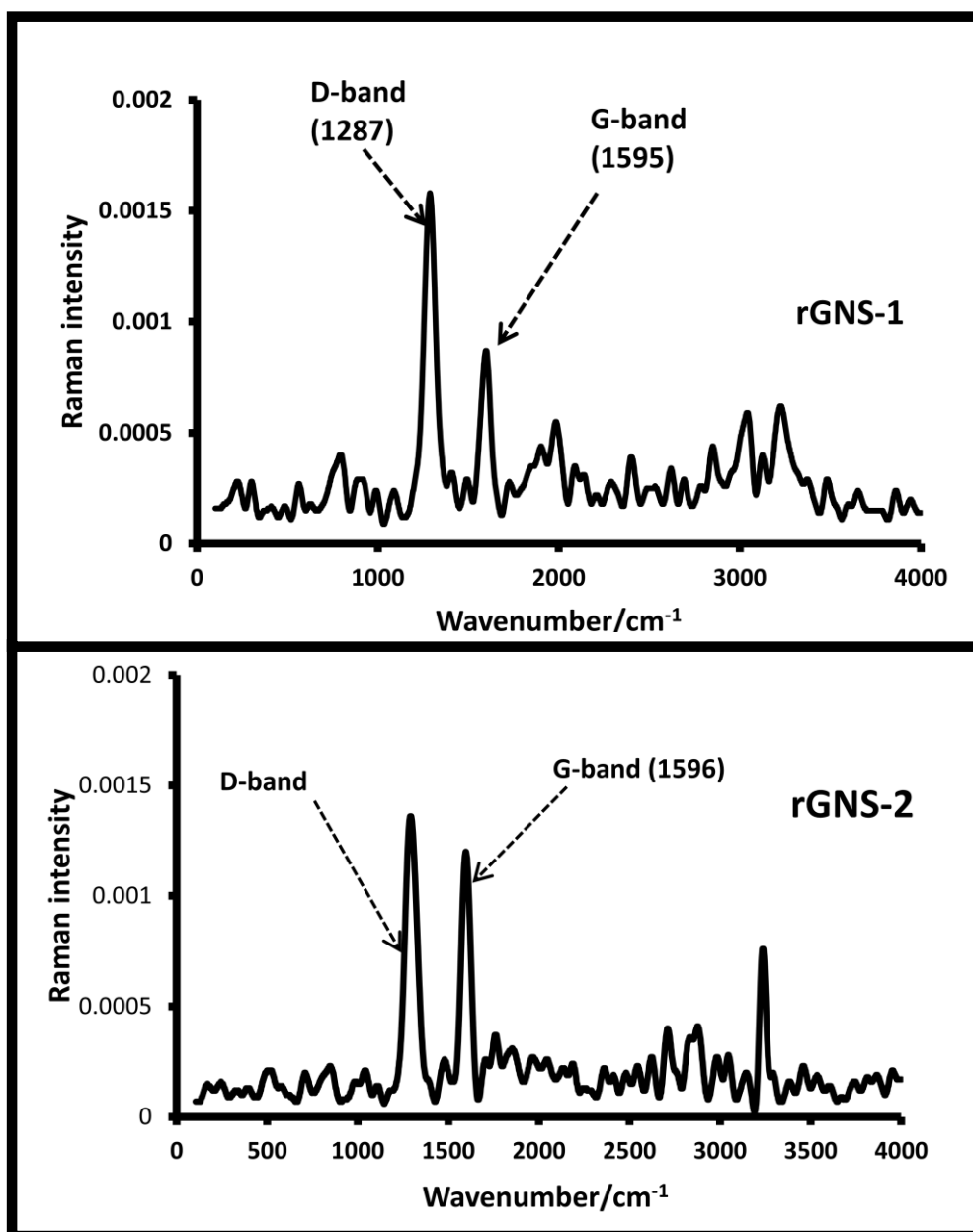


Fig. 3.6. Raman spectra of rGNS-1 and rGNS-2.

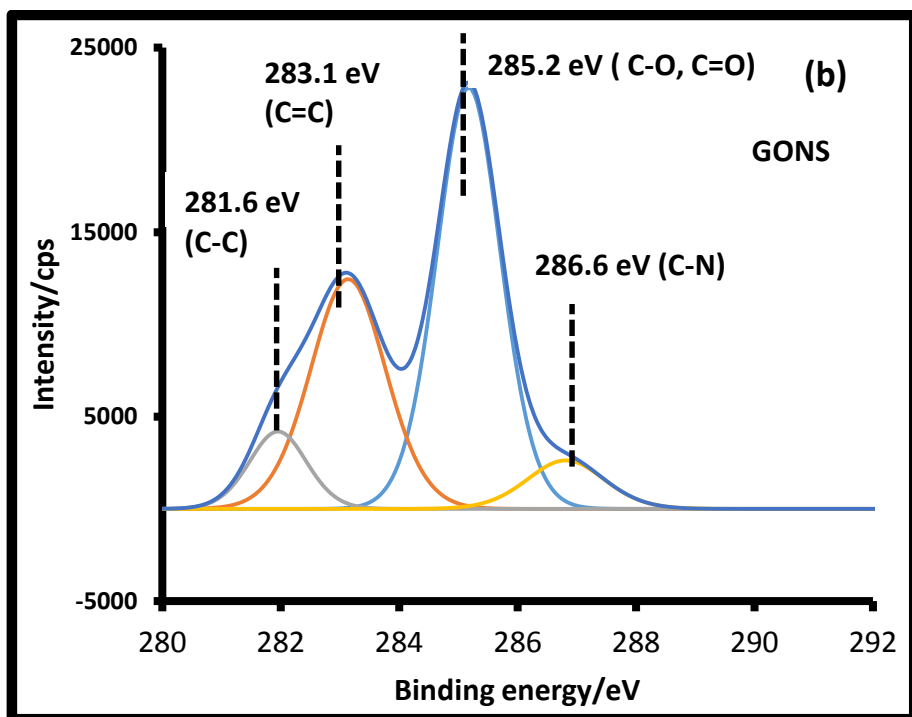
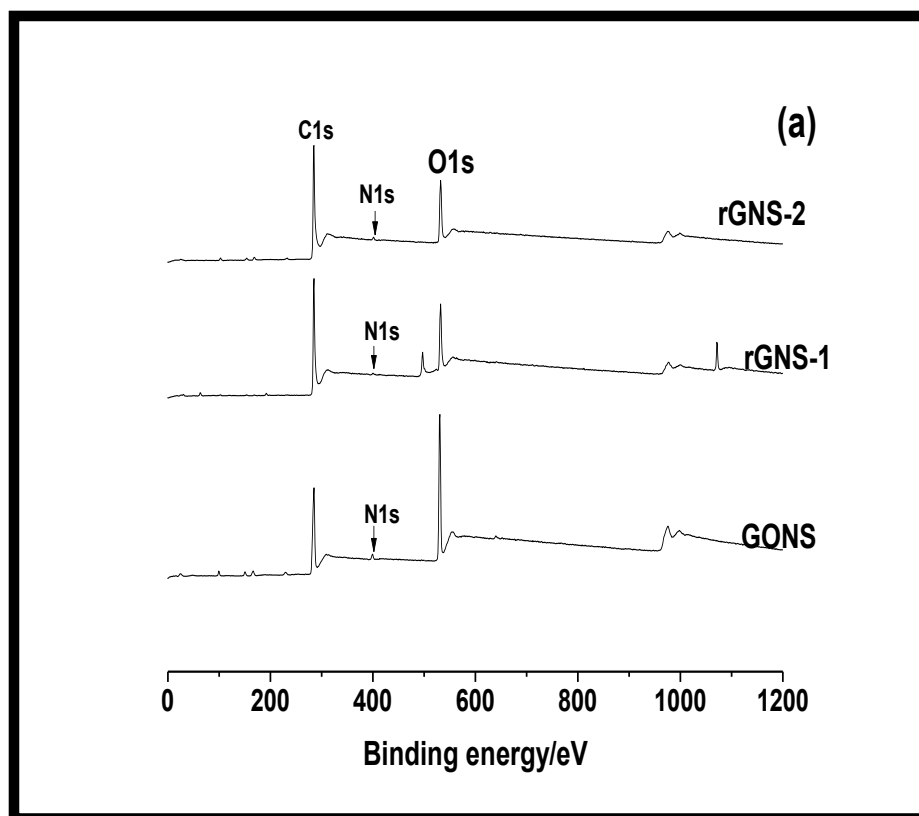
There is also an increase in intensity of the G-band for rGNS-2 (0.00119) relative to G-band for rGNS-1 (0.00087) showing an increase in the number of sp^2 domains upon treatment with H_2SO_4 . The average crystallite sizes of the reduced graphene were obtained using equation 3.1 [153];

$$L_a = 2.4 \times 10^{-10} \times \lambda_{laser}^4 \times \frac{I_G}{I_D} \quad (3.1)$$

where L_a = crystallite size, λ_{laser} = laser wavelength in nm, and I_G and I_D intensities of Raman G and D bands, respectively. These were found to be 559.6 nm and 351.6 nm for rGNS-1 and rGNS-2, respectively.

3.2.3. X-ray Photoelectron Spectroscopy (XPS) studies.

Since it is known that reduced graphenes have a small amount of oxygen functionalities at their surfaces, it is important to evaluate their surface chemical compositions by XPS. The wide scan XPS spectra, Fig. 3.7a were used to obtain atomic compositions and the data summarised in Table 3.2.



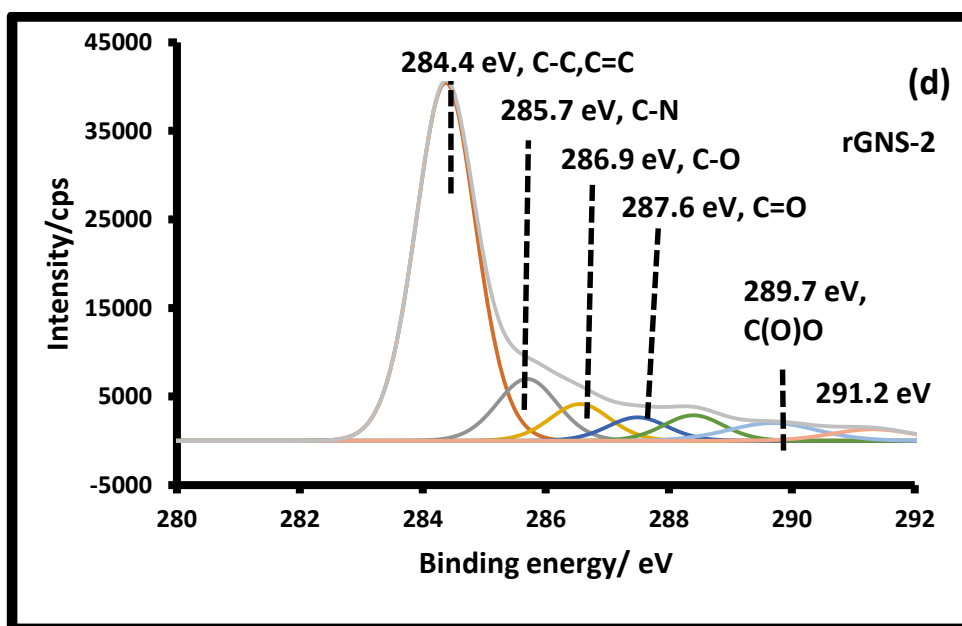
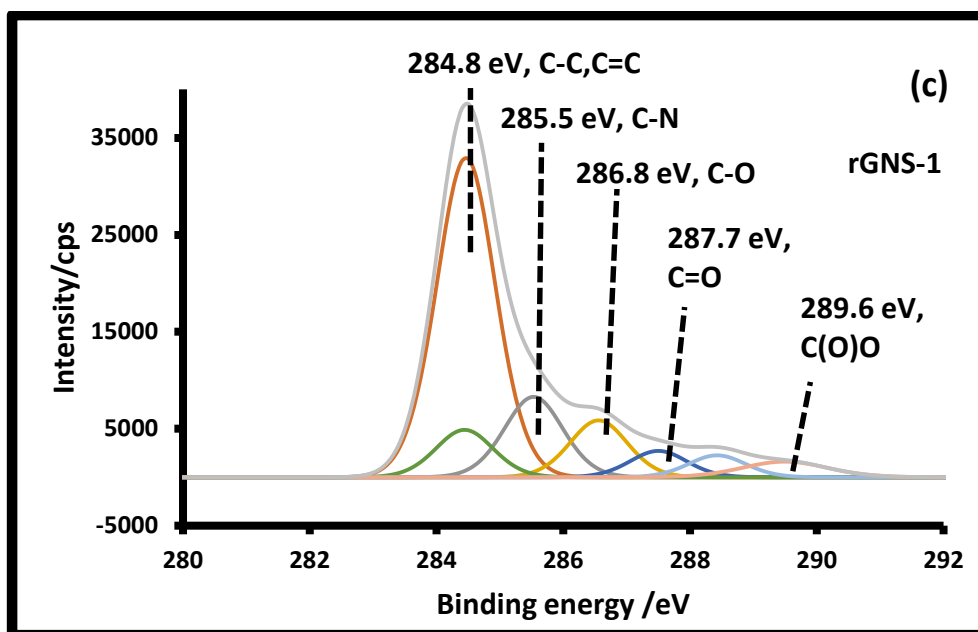


Fig. 3.7. (a) Wide scan XPS spectra for GONS, rGNS-1 and rGNS-2. High resolution deconvoluted C1s XPS peaks for (b) GONS, (c) rGNS-1 and (d) rGNS-2. All on glassy carbon plates.

The atomic concentration for oxygen in rGNS-1 and rGNS-2 were 16.67% and 15.12%, respectively, Table 3.2, and these values are close to those reported in literature [138]. Since XPS has different sensitivities towards different atoms, the following relative sensitivity factors were used for the determination of atomic concentrations for carbon, oxygen and nitrogen; 0.28, 0.78, and 0.48, respectively, Table 3.2.

Table. 3.2: A summary of XPS data of GONS, rGNS-1 and rGNS-2.

Peak	Position BE ^a (eV)	RSF ^b	Atomic conc. %	C:O ratio
GONS C1s	284.4	0.28	66.58	2
O1s	530.4	0.78	31.52	
N 1s	398.4	0.48	1.9	
rGNS-1 C1s	284.4	0.28	82.58	5
O1s	531.4	0.78	16.67	
N1s	399.4	0.48	0.75	
rGNS-2 C1s	283.9	0.28	83.95	6
O1s	530.9	0.78	15.12	
N1s	399.9	0.48	0.92	

^a BE= binding energy, ^bRSF= relative sensitivity factor.

The calculated C:O ratios for GONS, rGNS-1 and rGNS-2 were 2.0, 5.0, and 6.0, respectively. High C:O ratios imply low oxygen content, hence a better chemical sp² graphitic lattice structure restoration by H₂SO₄ as observed for rGNS-2. The N 1s peak was also observed in all cases but the relative atomic concentrations were very low i.e. 1.9% for GONS, 0.75% for rGNS-1 and 0.92% for rGNS-2, Table 3.2. Thus the

chemical reduction processes for GONS results in the elimination of some of the nitrogen inserted during preparation of graphene oxide. Fig. 3.7b-d shows the deconvolution of the XPS C1s peaks for GONS, rGNS-1 and rGNS-2. The deconvolution of C 1s XPS spectrum for GONS clearly shows a considerable amount of oxidation, Fig. 3.7b. The high resolution deconvoluted C1s XPS for the original GONS has four peaks due to carbon-carbon and carbon-oxygen functionalities, Fig. 3.7b. Though there are still some oxygen functionalities on the reduced graphenes (rGNS-1 and rGNS-2), their atomic concentrations were very low, Fig. 3.7c and d.

It is clear that after reduction, the carbon-carbon bonds were dominating, and oxygen functionalities appeared as small tailing peaks at the higher binding energy region (Fig. 3.7c and d). The reduction in peak intensity for oxygen functionalities in C1s XPS and the shift of XPS binding energies to higher values is an indication of good reduction of the GONS. From the C1s XPS, the carbon-carbon binding energy shifted from 283.1 eV in GONS (Fig. 3.7b) to 284.8 eV (Fig. 3.7c) and 284.4 eV (Fig. 3.7d) for rGNS-1 and rGNS-2, respectively. Such relatively large shifts on reduction of GONS have been observed before [154]. The C-O binding energies shifted from 285.2 eV in GONS to 286.8 eV and 286.9 eV in rGNS-1 and rGNS-2, respectively. The appearance of a π - π^* shake up signal at 291.2 eV for rGNS-2 is typically an indication of sp^2 hybridised carbon, and this is not well pronounced in rGNS-1 and absent in GONS. This is a further indication that GONS were chemically reduced, and the sp^2 structure was restored.

3.2.4. FTIR Spectra of GONS and reduced GNS.

From Fig. 3.8A the aromatic C=C bending at 1620 cm^{-1} and the carboxylic acid C=O stretch at 1731 cm^{-1} appear in the FTIR spectra of GONS spectrum. The observed the O-H stretch around 3204 cm^{-1} indicates the existence of either carboxylic acid or hydroxyl functional groups on GONS surface.

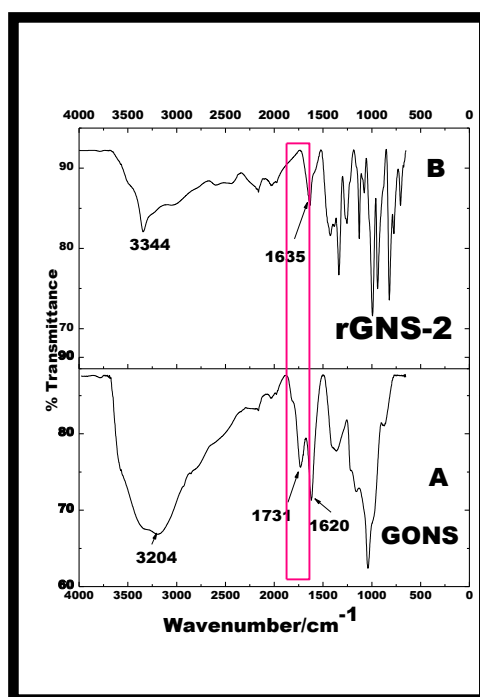


Fig.3.8. IR spectra (A) GONS and (B) rGNS-2.

The presence of such functionalities lowers the extended conjugation system for the individual graphene nanosheets and hence reduces electron transfer properties for GONS. A clear disappearance of a carboxylic acid C=O stretch at 1731 cm^{-1} was observed after reduction of GONS to rGNS. The intensity of the O-H stretch was also reduced in rGNS-2 at around 3344 cm^{-1} . Such changes in vibrational bands confirm successful removal of oxygen functionalities on the surface or edges of GONS. This

restores the extended conjugation system for graphene nanosheets, thereby promoting electron transfer properties.

3.2.5. XRD Patterns of rGNS-2 and GONS.

From the XRD patterns, Fig. 3.9, a typical [155] strong and sharp peak for GONS is observed at $2\theta = 9.68^\circ$ with a full width at half maxima (FWHM) value of 0.98° and d-value of $9.03 \text{ \AA}$. After reduction, a typical weak and broad peak near 25° is observed for rGNS-2 as observed before [156].

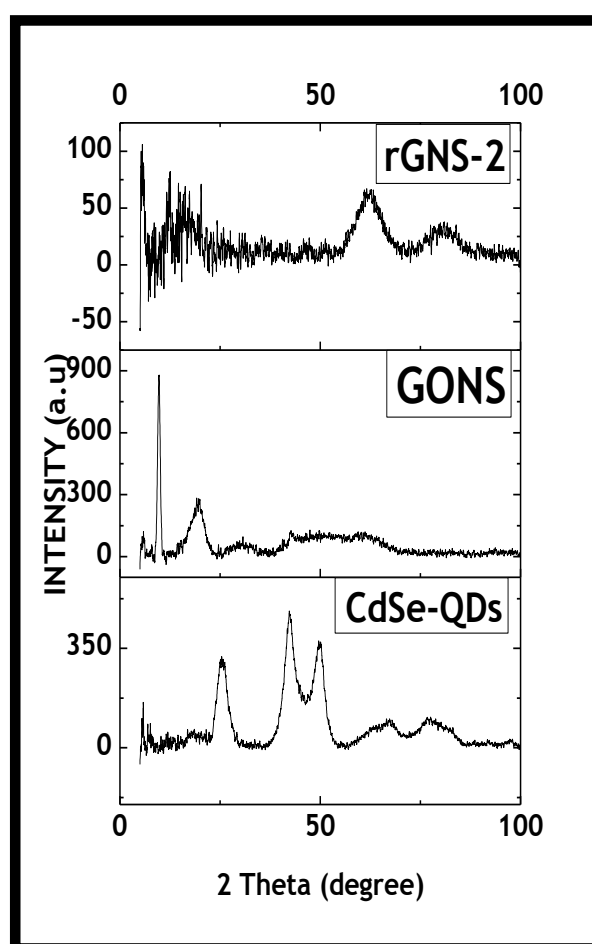


Fig. 3.9. XRD patterns of CdSe-QDs, GONS and rGNS-2.

Changes in the XRD patterns can be used as confirmation to the removal of the intercalating OH^- and the $-\text{COOH}$ groups from the GONS surface, resulting in the formation of rGNS-2, hence the observed smaller crystallite size for rGNS-2 (10.6 Å) than GONS (83.3 Å).

3.2.6. Transmission electron microscopy (TEM).

TEM analyses were performed to observe any morphological changes during formation of reduced graphene and to show the presence of MWCNTs in reduced graphene nanosheets. Fig. 3.10 shows the TEM images for GONS, rGNS-2 and rGNS-2-MWCNT.

The TEM micrographs clearly show the typical wrinkles for GONS, graphene nanosheets in rGNS-2, and MWCNTs embedded within the nanosheets indicating successful chemical reduction and incorporation of MWCNTs. The reduced graphene nanosheets show a more wrinkled and folded paper-like morphology than for GONS. The appearance of severe folding on rGNS-2 implies structural transformations and this is also an indication that stacked graphene nanosheets have been separated into either individual or few layered nanosheets.

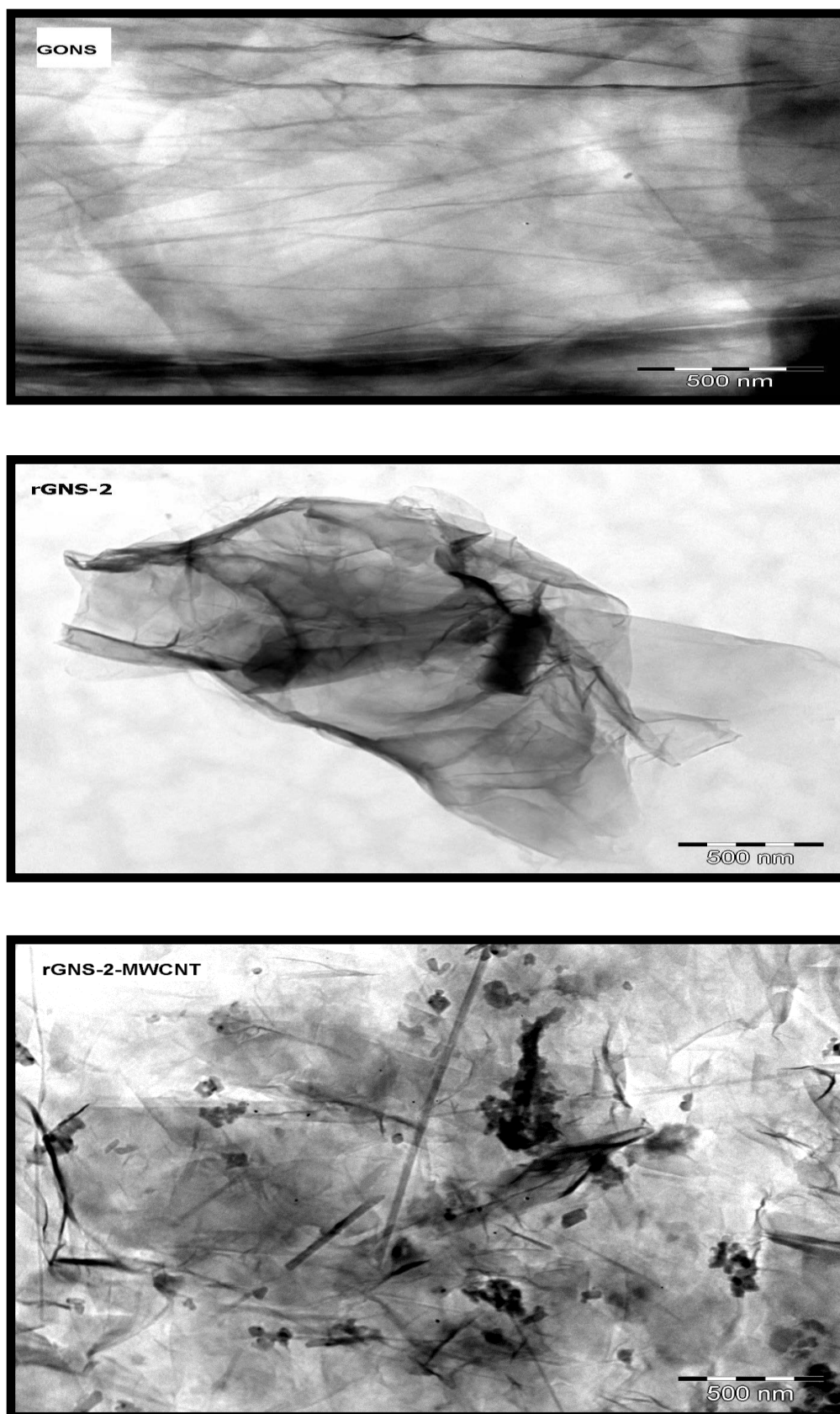
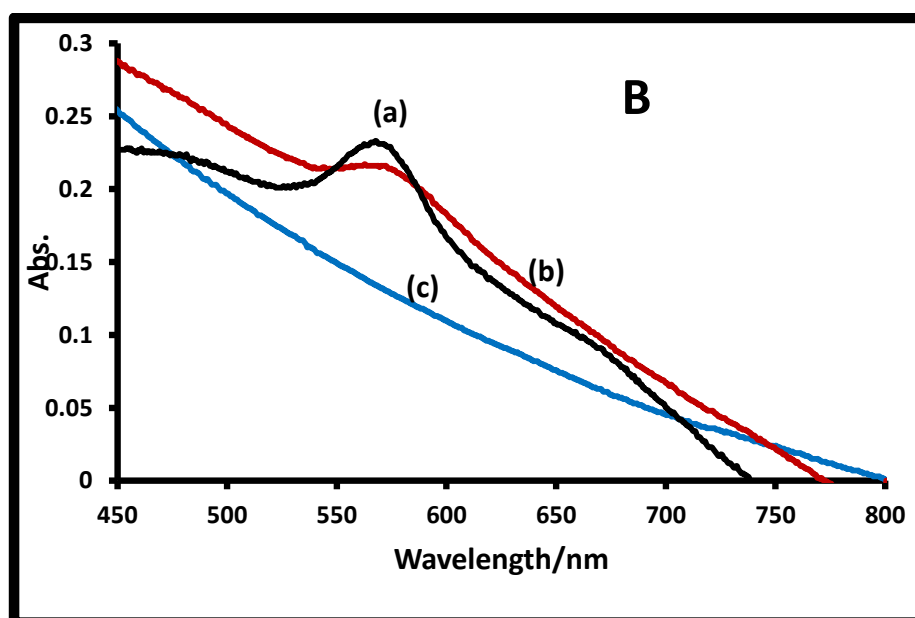
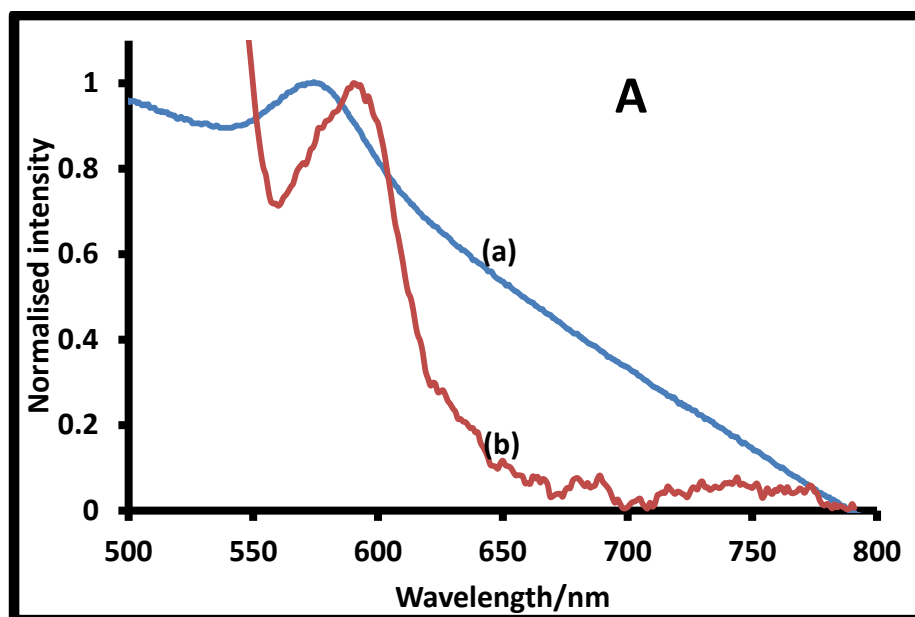


Fig. 3.10. TEM micrographs for GONS, rGNS-2 and rGNS-2-MWCNT.

3.2.7. UV/Vis.

For these studies the nanocomposites were sonicated in DMF to give their respective suspensions. Fig. 3.11A overlays the emission and absorption spectra of the quantum dots. Broad absorption peaks which extend to the near infrared region and narrow well-defined emission spectra are observed which are characteristic of quantum dots [159]. CdSe-QDs show an absorption peak at 568 nm (Table 3.1) which is also present in rGNS-2-CdSe-QDs (Fig. 3.11B (b)) confirming its successful incorporation into rGNS-2. rGNS-2 show no peak (Fig. 3.11B (c)).

CoPyPc shows a Q band peak at 676 nm (Table 3.1), and CoPyPc-rGNS-2 shows a slightly red shifted Q-band at 682 nm. There is a large blue shift in the Q band of - CoPyPc-rGNS-2-CdSe-QDs (at 672 nm) compared to CoPyPc alone, Table 3.1, Fig. 3.11C. The spectral shifts in MPc complexes in the presence of nanoparticles may depend on the orientation of the MPc on the nanoparticles as observed before for other dye systems [160].



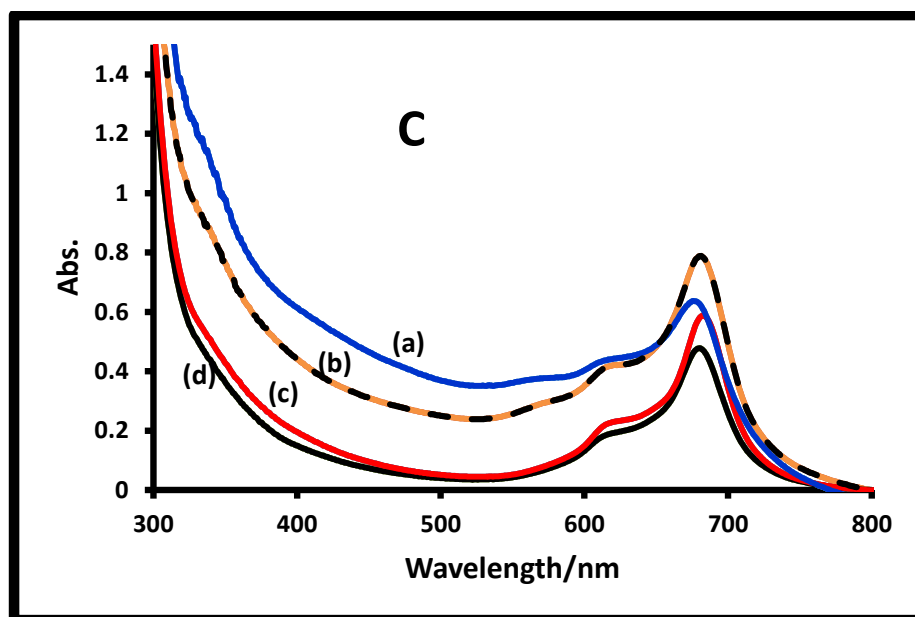


Fig. 3.11. (A) UV-VIS absorption (a) and emission spectra (b) of CdSe-QDs; (B) UV-VIS absorption spectra of CdSe-QDs (a), CdSe-QDs-rGNS-2 (b) and rGNS-2 (c); (C) CoPyPc-rGNS-2-CdSe-QDs (a), CoPyPc-CdSe-QDs (b), CoPyPc-rGNS-2 (c) and CoPyPc (d). Solvent = DMF.

3.3. Characterisation of QDs based nanocomposites.

3.3.1. TEM.

TEM was used to follow the changes in morphology or surface features during the preparation of CdSe-QD intercalated reduced graphene nanosheet (rGNS-2-CdSe-QDs). TEM image of CdSe-QDs show that they are spherical in nature, Fig. 3.12. The average size of the CdSe-QDs in Fig. 3.12 is 4 nm. When CdSe-QDs and rGNS-2 are physically mixed, the CdSe-QDs can be clearly seen on rGNS-2 as small spheres, Fig. 3.12.

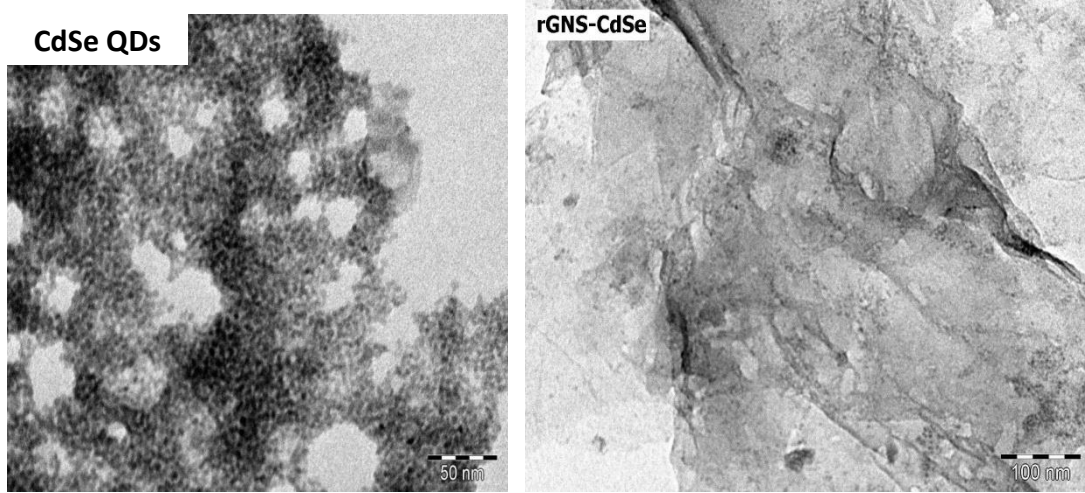


Fig.3.12. TEM images for CdSe-QDs and CdSe-QD-rGNS-2 nanocomposite.

3.3.2. XRD Patterns of CdSe-QDs, rGNS-2 and GONS.

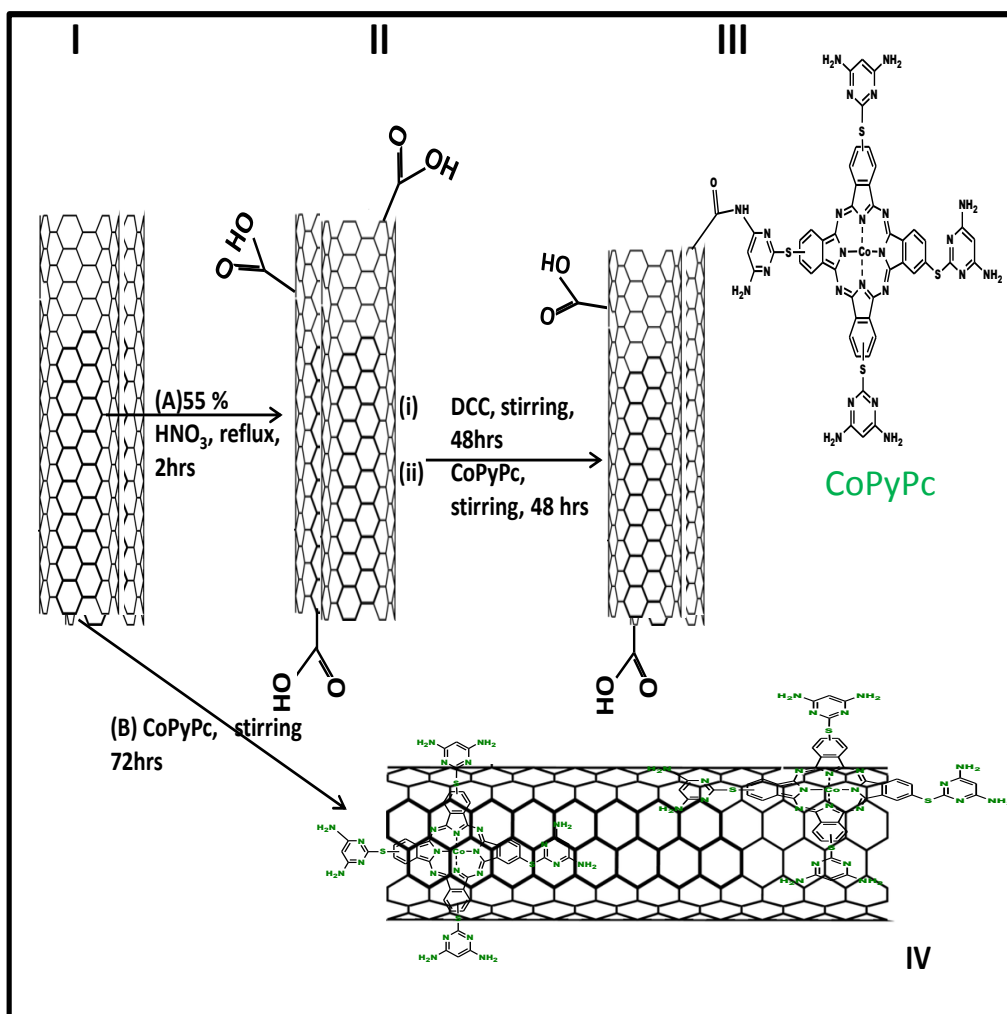
The XRD pattern of CdSe-QDs (Fig. 3.9) reveals three main peaks at diffraction angles $2\theta = 25.26^\circ$, 42.36° , and 49.99° , typical of CdSe-QDs [157]. The crystallite size of the CdSe-QDs was estimated using the Scherer Equation 3.2 [158].

$$d = 0.9\lambda / \beta \cos \theta \quad (3.2)$$

where d is the mean diameter of a quantum dot in nm, λ is the wavelength of the X-ray source ($1.5405 \text{ \AA}$), β is the full width at half maximum of the diffraction peak and θ is the angular position of the peak. The crystalline size of the CdSe-QDs was estimated to be 3.4 nm, and this is very close to the TEM average size (4 nm).

3.4. CoPyPc-MWCNTs nanocomposites.

Only CoPyPc (not CoTAPc) since the characterisation data is similar for both. CoTAPc was only mixed with MWCNTs and not covalently linked. MWCNTs were first made into MWCNTs-COOH to allow for covalent linkage with terminal -NH_2 groups of CoPyPc. The mixed nanocomposite was used for comparison with the covalently linked nanocomposite. The pathways for the formation of linked CoPyPc-MWCNT and adsorbed CoPyPc-MWCNT is shown in Scheme 3.3. CoPyPc-MWCNT (linked) was formed through amidation in the presence of DCC as an activating agent for carboxylic acid functional groups of MWCNT. The active carbodiimide ester group is readily attacked by the amino groups of the CoPyPc. Adsorbed nanocomposite was formed through π - π stacking. It is important to mention that covalently attached phthalocyanine molecules can additionally adsorb onto the MWCNT's surface by π - π stacking interaction [161] depending on the orientation of Pcs.



Scheme 3.3. A schematic representation for the preparation pathways for covalently linked MWCNT-CoPyPc nanocomposite (A) and adsorbed MWCNT-CoPyPc nanocomposite (B).

3.4.1. TEM and SEM.

TEM images (Fig. 3.13) clearly show some differences when MWCNT are either mixed or linked to CoPyPc. The linked nanocomposite show more structural material around the MWCNT and this is less pronounced in the mixed nanocomposite. This

can suggest that there are more CoPyPc molecules covalently attached to MWCNT than those which are adsorbed in the mixed nanocomposite, hence the expected higher activity for the linked nanocomposite.

TEM images of the MWCNT, Fig. 3.13D, clearly show the MWCNT bundles, which show increased black spots and a granulated structure (as highlighted on the image) following mixing with iodine doped CoPyPc.

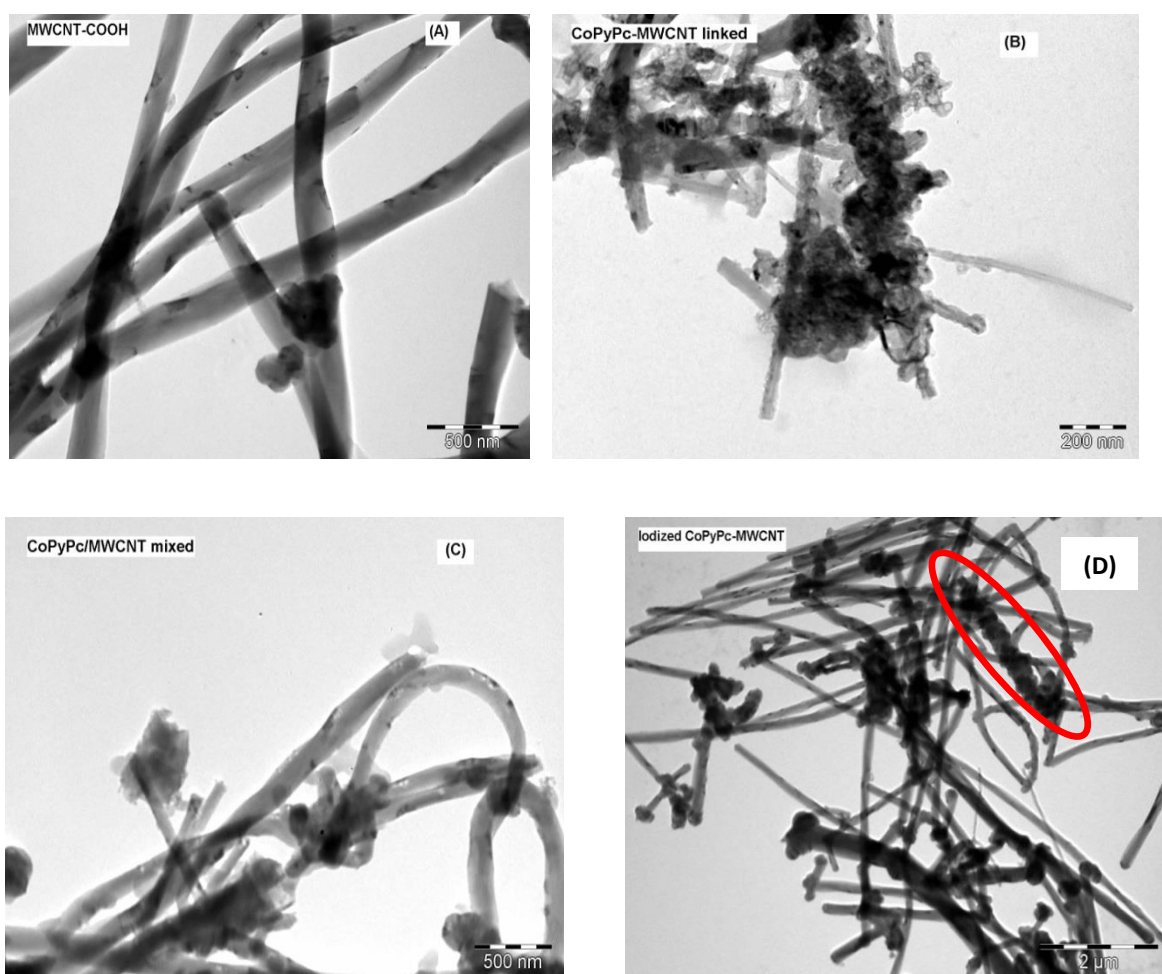


Fig. 3.13. TEM images for MWCNT-COOH (A), linked CoPyPc-MWCNT (B), mixed CoPyPc-MWCNT (C) and iodized CoPyPc-MWCNT. Highlighted area shows the difference in the presence of MWCNTs.

3.4.2. IR spectra.

FT-IR was used to confirm amide bond formation for the covalently linked nanocomposite. Fig. 3.14 clearly shows the differences in functionalities of the individual and nanocomposite materials. The vibrational assignments were according to literature [162,163]. MWCNT-COOH spectrum has a prominent feature around 1782 cm^{-1} which can be attributed to the carbonyl stretch of the free carboxylic acid group. The peak around 1400 cm^{-1} can be attributed to carboxylate (COO^-) band, an indication that some of the terminal carboxylic acid groups of the MWCNT are deprotonated. After reaction of MWCNT-COOH with DCC, followed by reaction with CoPyPc, an amide N-H band was observed at 1611 cm^{-1} and an amide C-N stretch at around 1408 cm^{-1} , confirming covalent linkage. These vibrations were not observed with the mixed nanocomposite, indicating a different mode of interaction other than covalent bonding.

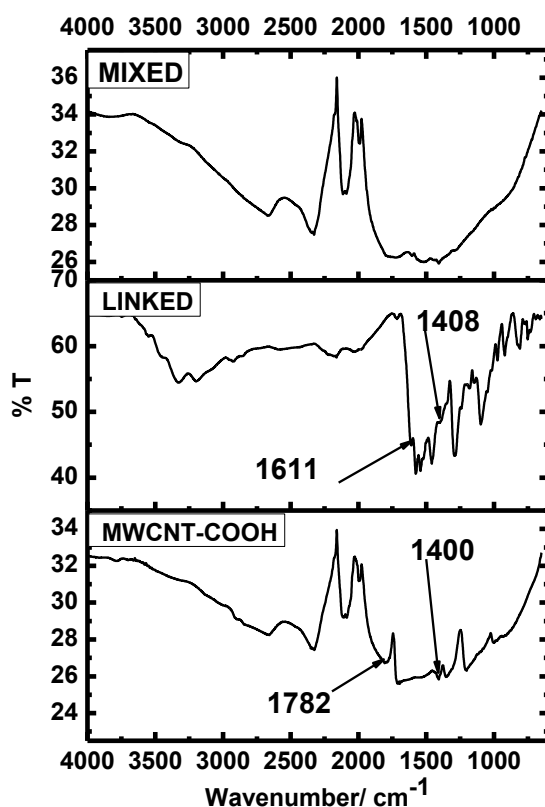


Fig.3.14. IR spectra for MWCNT-COOH, covalently linked and mixed CoPyPc-MWCNT nanocomposites.

3.4.3. UV-Vis absorption spectra.

The Q-bands of CoPyPc was red shifted in the presence of MWCNT (either linked or mixed), Fig. 3.15. However, there was more red-shifting observed in mixed than linked nanocomposites. The mixed nanocomposite for CoPyPc showed a red-shift of 6 nm in comparison to the linked nanocomposites or CoPyPc alone. The red shift of the Q-band in the spectra of nanocomposites gives evidence to the reduction of HOMO-LUMO energy gap [109], caused by the presence of MWCNT. The destabilization/reduction of the HOMO-LUMO energy gap is an intrinsic property of a material necessary for electrocatalysis. Furthermore, the spectral shifts in MPC

complexes in the presence of MWCNT may depend on the orientation of the MPc on the MWCNT as stated above [160]. The red shifting in the Q band may also be due to π - π stacking interaction for the mixed conjugates. The fact that there is a red shifting for the covalently linked conjugates, indicates that in addition to the covalent interaction there is some π - π stacking interaction.

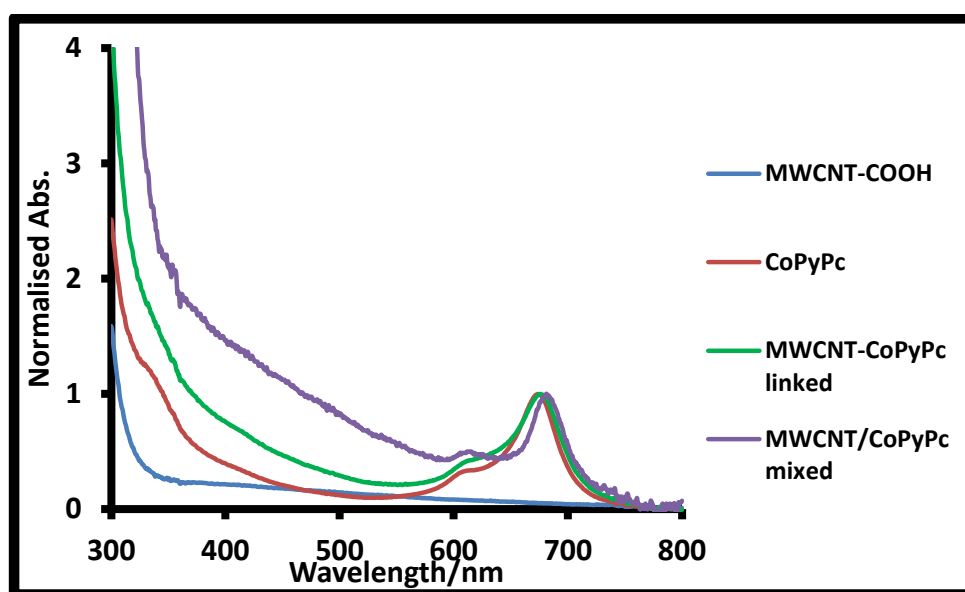


Fig. 3.15. UV-Vis spectra of individual (MWCNT-COOH and CoPyPc), and nanocomposite (linked and mixed) catalysts in DMF.

3.5. Conclusion.

Characterization of the iodine-doped CoPyPc complex was carried out and it proved the presence of iodines on the doped CoPyPc. XPS further confirmed the presence of iodine and EPR proved the presence of radicals. Visual and physical characterisations also proved successful reduction of GONS as well as incorporation of intercalating agents (MWCNTs and CdSe-QDs) in between rGNS. FT-IR confirmed

amide bond formation for the covalently linked nanocomposite. Both linked and mixed nanocomposites resulted in red shifting of the Q-band of MPc. The mixed nanocomposites resulted in more red-shifting of the Q-band than the linked nanocomposites.

Chapter Four: Electrode modification and Characterisation.

This chapter focuses on electrode modification and characterisation using various nanomaterials and their nanocomposites.

4.1. CoTAPc based electrodes.

Table 4.1 shows a list of the electrode modifiers employed in this work.

Table 4.1: A list of MPc based electrode modifiers and their applications evaluated in this work.

Electrode modifiers	Application
<u>(a) CoTAPc based electrodes and individual components.</u>	
CoTAPc-MWCNT (sequential)	l-cysteine electrooxidation/ PQ reduction
CoTAPc-MWCNT (mixed)	l-cysteine electrooxidation/ PQ reduction
GONS	Paraquat reduction
rGNS-1	Paraquat reduction
rGNS-2	Paraquat reduction
rGNS-2-MWCNT (mixed)	Paraquat reduction
CoTAPc	Paraquat reduction
CoTAPc-rGNS-2 (sequential)	Paraquat reduction
CoTAPc-rGNS-2-MWCNT (sequential)	Paraquat reduction
Poly-CoTAPc-GCE	l-cysteine electrooxidation

Poly-CoTAPc-MWCNT-GCE	l-cysteine electrooxidation
CdSe QDs	ORR
<u>(b) CoPyPc and CoPc based electrodes, and individual components.</u>	
CoPyPc-rGNS-2 (sequential)	ORR
rGNS-2-CdSe QDs (mixed)	ORR
CoPyPc	ORR/ l-cysteine electrooxidation
CoPyPc-rGNS-2-CdSe QDs (sequential)	ORR
CoPyPc-MWCNT (covalently linked)	ORR/ l-cysteine electrooxidation
CoPyPc-MWCNT-COOH (mixed)	ORR/ l-cysteine electrooxidation
MWCNT-COOH	ORR/ l-cysteine electrooxidation
Iodine doped CoPyPc	ORR
Iodine doped CoPyPc-MWCNT (sequential)	ORR
Iodine doped CoPyPc	ORR
Poly-CoPyPc-GCE	l-cysteine electrooxidation
Poly-CoPyPc-MWCNT-GCE	l-cysteine electrooxidation
CoPc based electrodes	
Iodine doped CoPc	ORR
CoPc	ORR

4.1.1. Sequential and premixed MWCNT-CoTAPc modified electrodes.

MWCNTs have been used for the detection of analytes [164]. The aim of this part of work is to determine the influence of the MWCNTs (due to conductive nature) on the catalytic behaviour of CoTAPc. Hence, the MWCNTs were not acid functionalized. However, in some other applications of this work, MWCNTs were acid functionalized to allow for covalent linkage to MPc (Scheme 3.3). The influence of the method of nanocomposite preparation (premixing vs. sequential) on the electrocatalytic behaviour is also evaluated.

4.1.1.1. SEM.

SEM images (Fig. 4.1) show that sequential modification procedure has more exposed bare surface area unlike the premixed modified surface which is almost completely covered. These bare areas are also exposed to the redox mediator hence can contribute to anodic/cathodic peak currents.

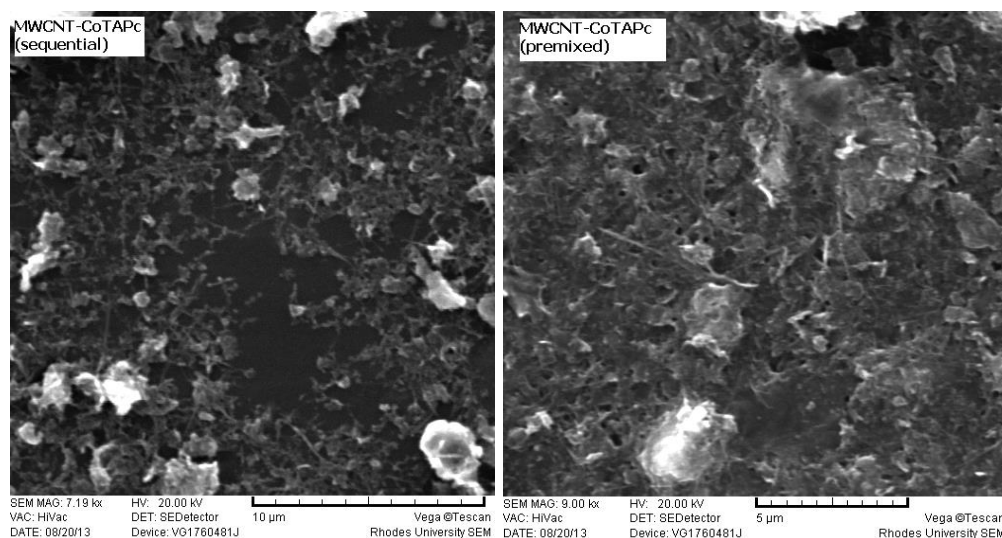


Fig. 4.1. SEM images for CoTAPc-MWCNT: sequential (top) and CoTAPc-MWCNT: mixed (bottom) on a glassy carbon plate.

4.1.1.2. Cyclic voltammetry (CV).

Fig. 4.2 shows comparative CVs for the bare and modified glassy carbon electrodes obtained in the presence of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple. The CVs shown in Fig. 4.2 represent the second scans of the multiple scans performed. The peaks for the first scans were not well defined, and the rest of the scans were almost the same as the second scans. Peak currents for the modified surfaces (Fig. 4.2b and c) are several times higher than the bare glassy carbon electrode. However, noteworthy from these CVs for modified surfaces is the higher anodic and cathodic peak currents when the drops of MWCNTs and CoTAPc are added separately (Fig. 4.2c, CoTAPc-MWCNT (sequential)) on glassy carbon electrode than when premixed (Fig. 4.2b, CoTAPc-MWCNT (mixed)).

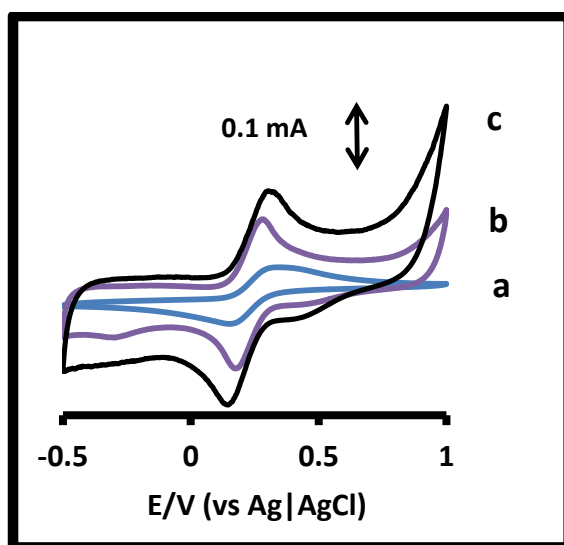


Fig. 4.2. Comparative cyclic voltammograms of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 1 M KCl using bare GCE (a), CoTAPc-MWCNTs (mixed) (b), and CoTAPc-MWCNTs (sequential) (c). Scan rate = 100 mV/s.

Thus, CoTAPc-MWCNT (sequential) shows higher currents. This is due to the fact that catalysis occurs on the CoTAPc (which should be the top layer) with the bottom layer (MWCNTs) providing transmission of electrons. Furthermore, the capacitive/nonfaradaic currents for (Fig. 4.2c) are much higher than those for (Fig. 4.2b), an indication of strong interaction between the modifiers and the bare glassy carbon electrode. The anodic to cathodic peak (ΔE) separation was however larger for CoTAPc-MWCNT (sequential) at 0.15 mV compared to CoTAPc-MWCNT (mixed) at 0.07 mV, Table 4.2, suggesting better electron transfer kinetics for latter even though it shows lower currents.

Since SEM showed that the electrodes have bare and modified parts, peak currents are therefore a result of two influences i.e. modified parts (fast electron transfer) and bare parts (slow electron transfer), leading to peak broadening and widening of peak potential separation for sequential. It is clear that despite having some unmodified parts for the sequential treatment, it retained better catalytic currents and sensitivity. This makes the sequential treatment a better procedure to be employed for fabrication of a sensor platform. The reverse where CoTAPc was the bottom layer and MWCNTs was the top layer was found to give very weak catalytic behaviour and was not explored further. Surface coverage studies were not explored since CoTAPc peaks were not clear or well pronounced.

Table 4.2: A summary of ΔE and R_{ct} values for the different CoTAPc electrode surfaces.

Electrode surface	$E_{pa} - E_{pc}$ for $Fe(CN)_6^{3-/4-}$	R_{ct} (Ω) for $Fe(CN)_6^{3-/4-}$ (#)
Bare GCE	0.08	10.6 (2.61%)
GONS-GCE	_____a	11.1(2.30 %)
rGNS-1-GCE	0.39	9.3 (1 23 %)
rGNS-2-GCE	0.15	5.0 (3.12 %)
rGNS-2-MWCNT-GCE (mixed)	0.14	1.8 (1.03 %)
CoTAPc-GCE	0.08	2.0 (7.71 %)
CoTAPc-MWCNT-GCE (sequential)	0.15	1.56 (22 %) ^b
CoTAPc-MWCNT-GCE (mixed)	0.07	1.98 (22 %) ^b
CoTAPc-rGNS-2-GCE (sequential)	0.12	5.3 (2.83 %)
CoTAPc-rGNS-2-MWCNT-GCE (sequential)	0.08	1.4 (3.96 %)

^a no peak. ^b R_{ct} values obtained in 0.05 mM l-cysteine in pH 4 buffer. [#]Values in brackets are the relative errors.

4.1.1.3. Scanning electrochemical microscopy (SECM).

SECM was employed to probe the conducting behaviour of the modified surfaces. Fig. 4.3 shows changes in tip current as the ultra-micro electrode (UME) tip approaches the substrate in a feedback mode experiment in the presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox mediator. When a sufficiently positive potential is applied to the tip, the oxidation of Fe^{2+} to Fe^{3+} occurs, and the rate is governed by the diffusion of Fe^{2+} to the UME tip surface.

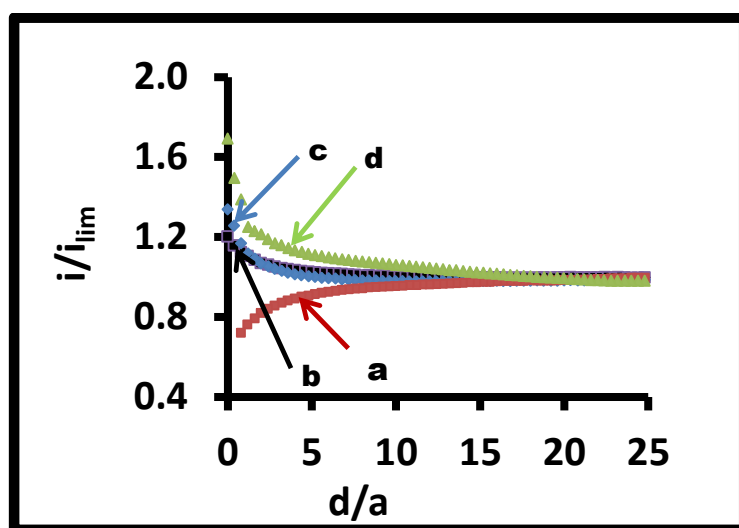


Fig.4.3. Approach curves to non-conducting Teflon (a), bare glassy carbon plate (b), CoTAPc-MWCNTs (mixed) (c), and CoTAPc-MWCNTs (sequential) (d). d/a = ratio of tip-substrate distance to UME tip radius.

When the tip is closer to a conductive substrate surface, the Fe^{3+} diffuses to the substrate where it is reduced back to Fe^{2+} [134,135]. This results in an additional flux of Fe^{2+} to UME tip and hence the observed increases in tip current (positive feedback) for bare glassy carbon plate and the modified surfaces. The tip currents for the CoTAPc-MWCNT (sequential) modified surface (Fig. 4.3d) are higher than the

premixed surface modification (Fig. 4.3c). This is the same trend observed for the anodic peak currents in cyclic voltammetry. The approach curves were obtained at the same tip-substrate separation micro-distance.

Fig. 4.4 shows 2D and 3D SECM images for the modified surfaces. The 2D contour plot shown in Fig. 4.4A clearly shows conductivity of the CoTAPc-MWCNT (sequential) modified glassy carbon plate (yellow/orange area) against the bare surface (blue area). The 3D plots show larger tip currents (~ 21 nA) for CoTAPc-MWCNT (sequential) (Fig. 4.4B) compared to 9.6 nA of the CoTAPc-MWCNTs (mixed), Fig. 4.4C. Thus it is expected that the former will show better catalytic activity, as will be in the next chapter.

The surface topography for the 3D images is not smooth. This can be attributed to the fact that MPc and the MWCNTs on the electrode have different electrical properties. However there is a clear distinction in surface roughness between the two modified surfaces. The premixed modified surface (Fig. 4.4C) is less rough with the nanoparticles more evenly distributed than the sequential modified surface (Fig. 4.4B) which shows some spikes in tip current intensities.

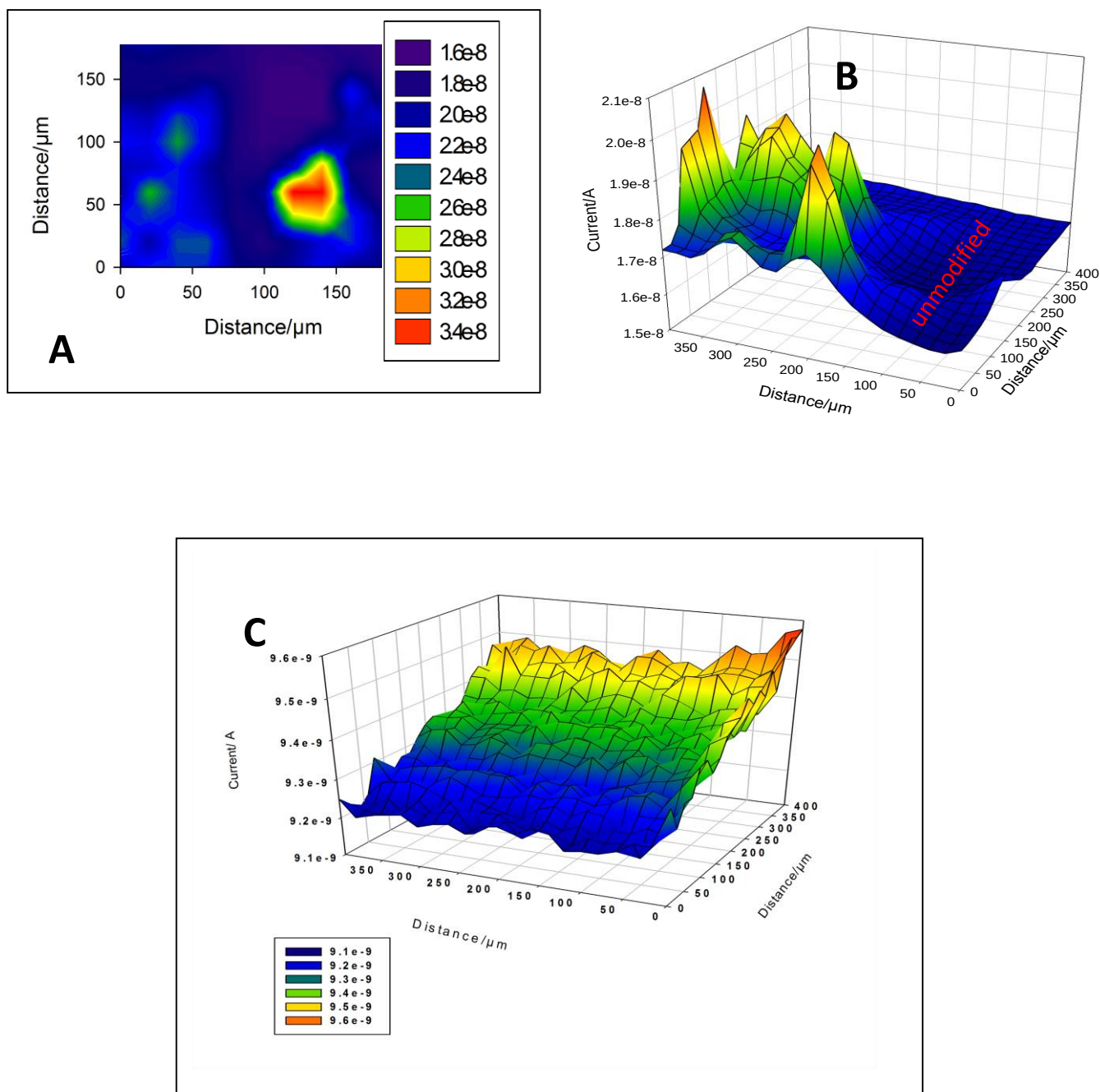


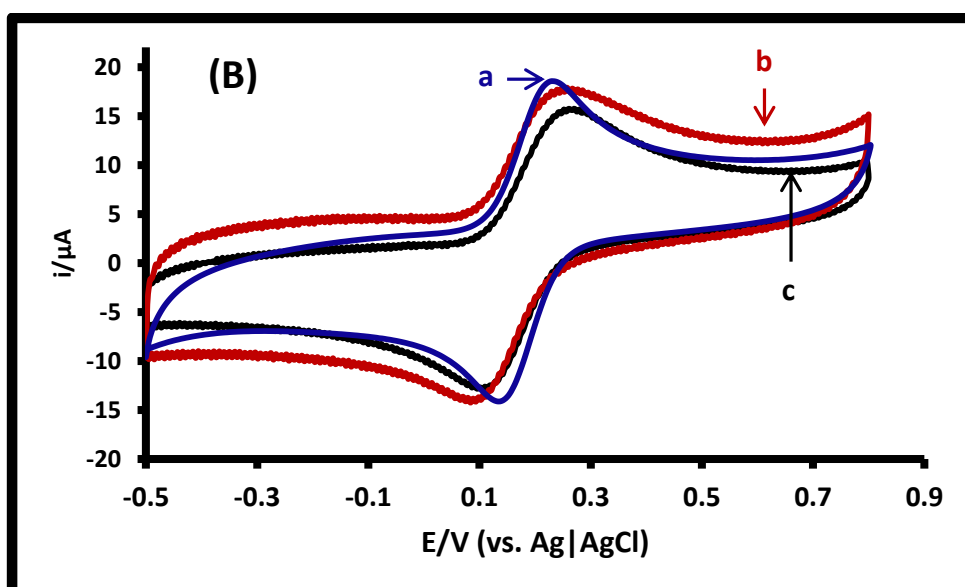
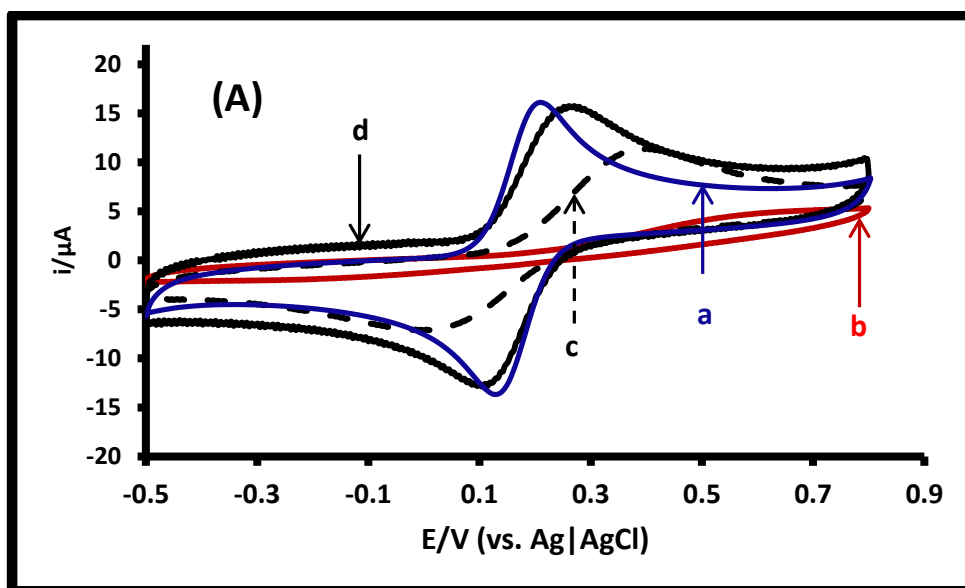
Fig. 4.4. SECM images: 2D contour plot for CoTAPc-MWCNTs (sequential) (A) and 3D plot for (B) CoTAPc-MWCNTs (sequential) and (C) CoTAPc-MWCNTs (mixed) using 15 μm UME in 1 M KCl.

4.1.2. CoTAPc-rGNS-MWCNT nanocomposites (sequential).

The electrodes were modified in a sequential manner in this section due to its superiority discussed above and are listed as sequential in Tables and figures. As stated above, the MPc was placed on top of the nanocomposites in all cases. As stated above, experiments where MPc was placed on the electrode first followed by the nanocomposites resulted in low catalytic currents relative to when MPc is placed on top. It is against this background that placing MPc on top was preferred in this study.

4.1.2.1. Cyclic voltammetry studies.

Cyclic voltammetry studies of the electrodes in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl are shown in Fig. 4.5. All the electrodes containing reduced GNS show higher non-faradaic currents within the potential window -0.05 V to -0.5 V. No peaks were observed on GONS due to lack of conductivity. The conductivity improved for rGNS-1 (following deoxygenation, hence partial restoration of sp^2 structure) but with a much larger cathodic to anodic peak potential ($\Delta E = 0.39$ V) than for rGNS-2 ($\Delta E = 0.15$ V), Table 4.2, showing superior conductivity of the latter electrode. It is noted also that NaBH_4 reduction alone does not remove most of the oxygen functionalities, thus further treatment with 98% H_2SO_4 resulted in improvement in ΔE .



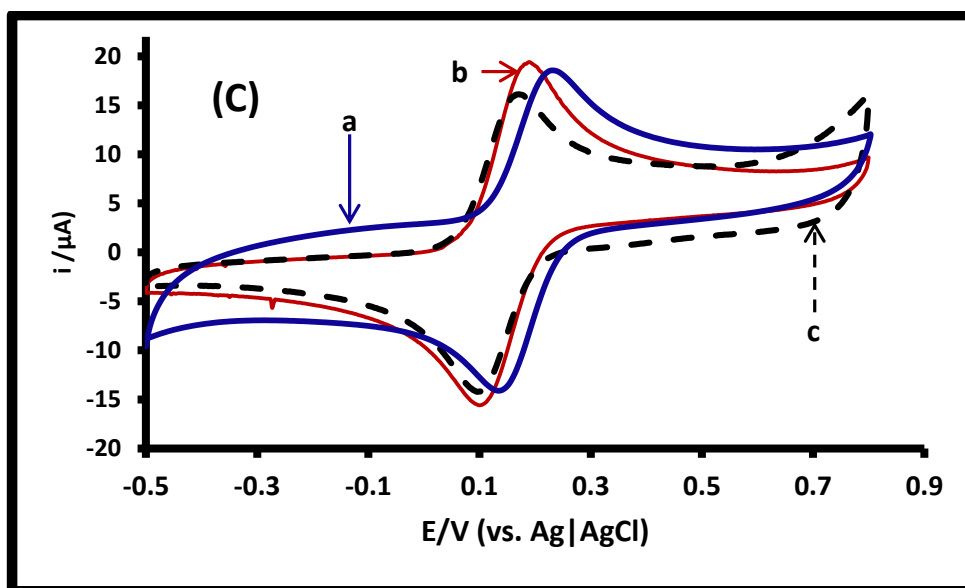
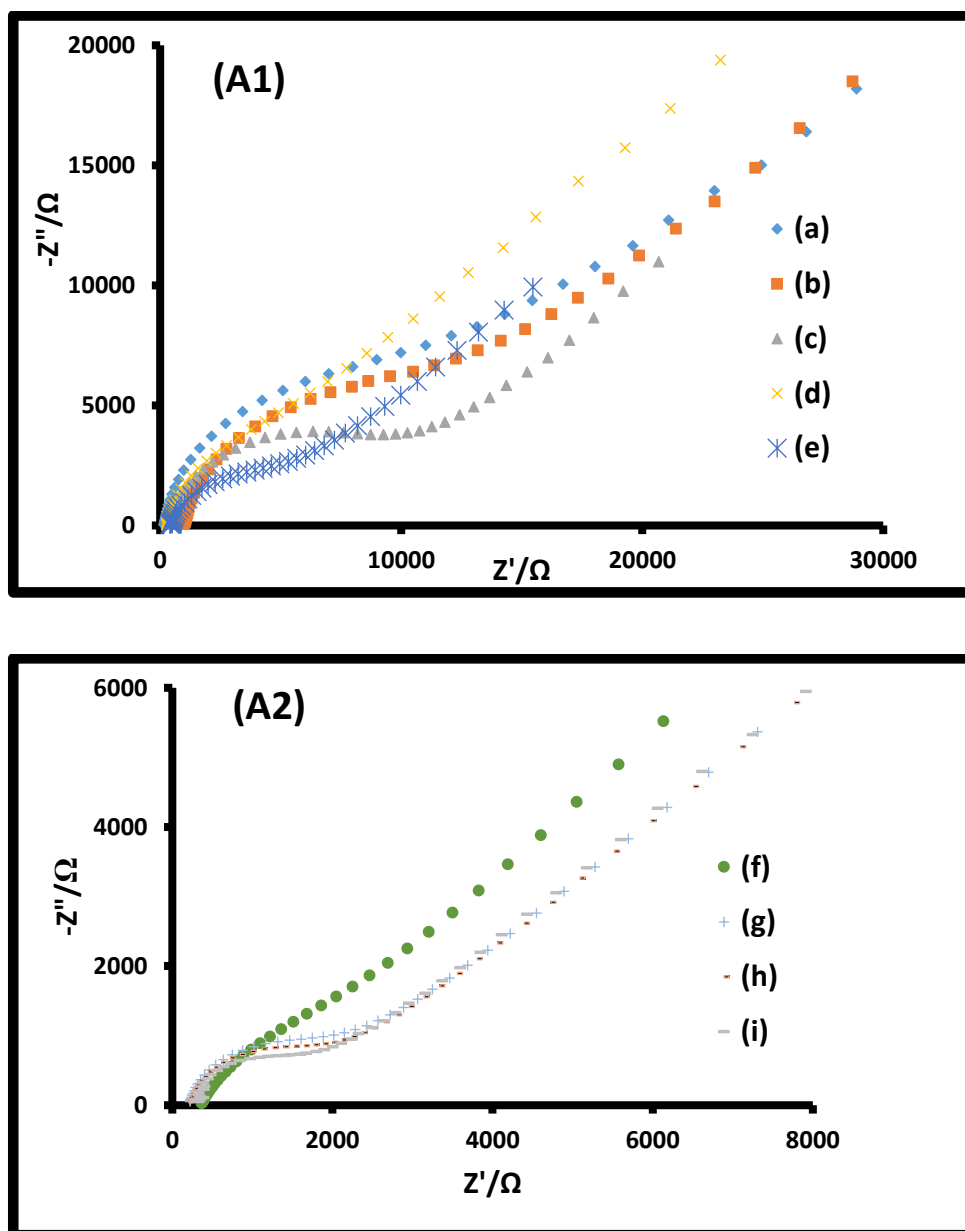


Fig. 4.5. Cyclic voltammograms (CVs) of 1mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1M KCl using (A) bare GCE (a), GONS-GCE (b), rGNS-1-GCE (c) and rGNS-2-GCE (d); (B) CoTAPc-rGNS-2-MWCNT-GCE (sequential) (a), rGNS-2-MWCNT-GCE (mixed) (b), and CoTAPc-rGNS-2 (sequential) (c) and (C) CoTAPc-rGNS-2-MWCNT-GCE (sequential) (a), CoTAPc-MWCNT-GCE (sequential) (b), and CoTAPc-GCE (c). Scan rate = 100 mV/s.

The trend in terms of ΔE for the $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple is as follows: rGNS-1-GCE (0.39 V) > rGNS-2-GCE (0.15 V) $\approx$ rGNS-2-MWCNT-GCE (0.14 V) > CoTAPc-rGNS-2-GCE (0.12 V) > CoTAPc-MWCNT-GCE (0.08 V) = CoTAPc-GCE (0.08 V) = CoTAPc-rGNS-2-MWCNT-GCE (0.08 V) $\approx$ Bare (0.08 V). The trend shows that CoTAPc-rGNS-2-MWCNT has better electrochemical properties than individual components.

4.1.2.2. EIS studies.

The electrochemical behaviour of our graphene modified surfaces was further examined by EIS, Fig. 4.6. EIS was done here as an example, hence was not explored with mixed or sequential modified CoTAPc-MWCNT electrodes discussed above.



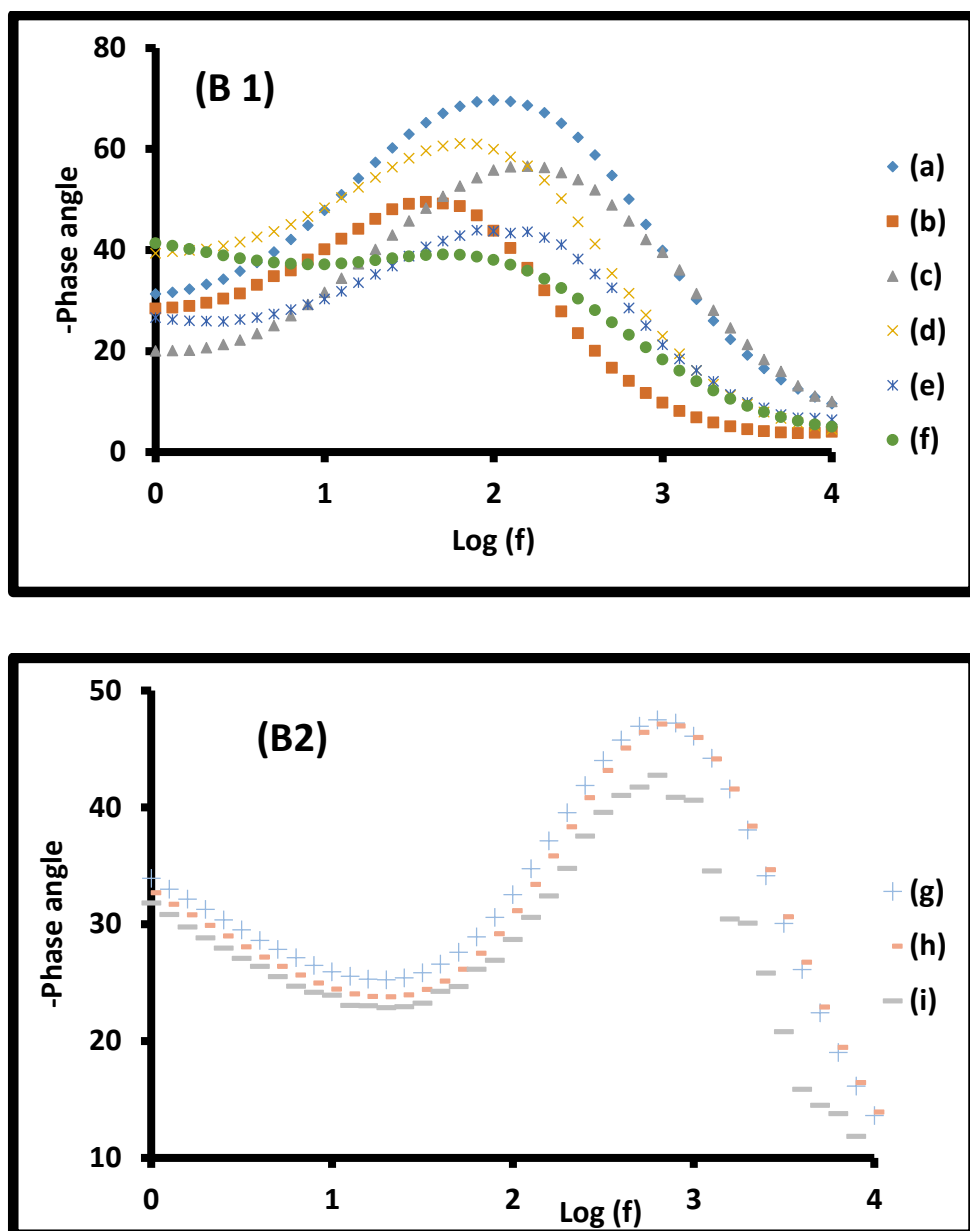


Fig. 4.6. (A) Nyquist and (B) Bode plots for GONS-GCE (a), bare GCE (b), rGNS-1-GCE (c), rGNS-2-GCE (d), rGNS-2-MWCNT-GCE (mixed) (e), CoTAPc-rGNS-2-MWCNT-GCE (sequential) (f), CoTAPc-GCE (g), CoTAPc-rGNS-2-GCE (sequential) (h), CoTAPc-MWCNT-GCE (sequential) (i).

The EIS studies were carried out in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl at the half-wave potential of 0.15 V. A The Randles equivalent circuit ($R_1(Q_1[R_2W_1])$) was used to

model the electrochemical cell, where R_s is the solution resistance, R_{ct} is the charge transfer resistance and C_{dl} is the double layer capacitance. The Nyquist plot is divided into two frequency regions, the kinetically controlled (high frequency) region where the semi-circle is observed and the diffusion controlled (low frequency) region where the Warburg line is observed. On a Nyquist plot the infinite Warburg impedance appears as a diagonal line. The diameter of the semi-circles in Fig. 4.6A relates to the resistance to charge transfer, and the greater the diameter of the semi-circle the greater the R_{ct} value and consequently slow electron transfer. Typical R_{ct} values range from a few Ohms for very fast reaction kinetics to greater than 10 G Ω for very slow reaction kinetics at the electrode surface. GONS has the largest R_{ct} value compared to all other surfaces, Table 4.2, and this is consistent with the lack of peaks on GONS in Fig. 4.5.

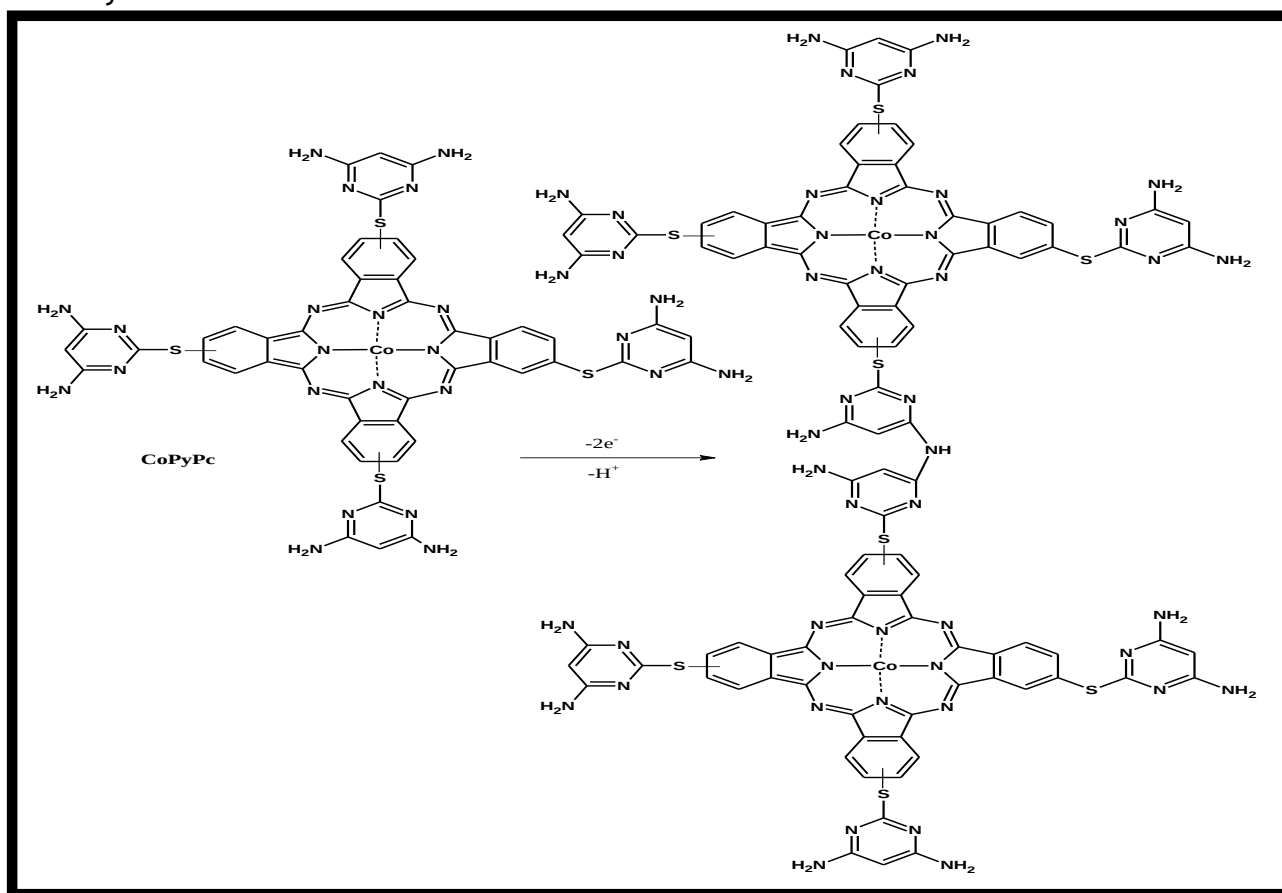
On reduction of GONS to make rGNS-1 and rGNS-2 there was a decrease in R_{ct} values from 11.1 k Ω (for GONS) to 9.3 k Ω (for rGNS-1) and 5.0 k Ω (rGNS-2), respectively, Table 4.2. The trend in terms of R_{ct} for the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple is as follows: GONS (11.1 k Ω) > Bare GCE (10.6 k Ω) > rGNS-1-GCE (9.3 k Ω) > CoTAPc-rGNS-2-GCE (5.3 k Ω) > rGNS-2-GCE (5.0 k Ω) > CoTAPc-GCE (2.0 k Ω) > rGNS-2-MWCNT-GCE (1.8 k Ω) > CoTAPc-MWCNT-GCE (1.7 k Ω) > CoTAPc-rGNS-2-MWCNT-GCE (1.4 k Ω).

Again, the trend shows that the presence of MWCNT and CoTAPc in the nanocomposite improves the activity of reduced graphene nanosheets. Information from the Bode plots (Fig. 4.6B) also confirms that all the surfaces have different

behaviours since their phase angles are shifted to different frequencies. On a Bode plot, the Warburg impedance exhibits a phase shift of 45° . Except for GONS (69°), bare (61°) and rGNS-1 (56°), all other surfaces show phase shifts very close to 45° .

4.1.3. Poly CoTAPc compared with poly CoPyPc.

Scheme 4.1 shows the possible oxidative coupling for the formation of poly-CoPyPc.



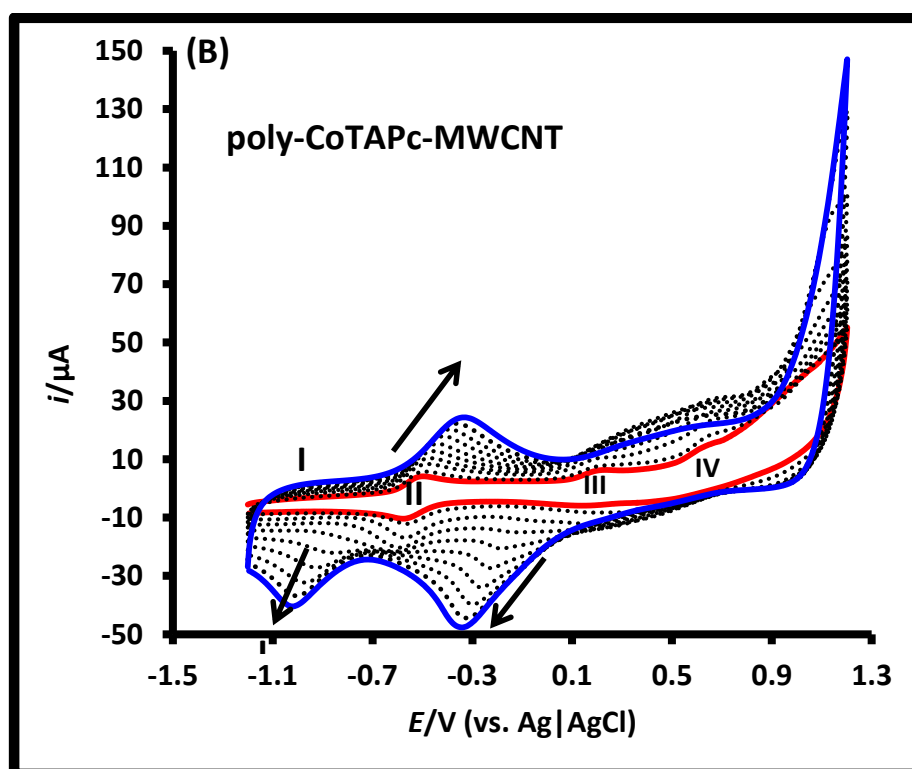
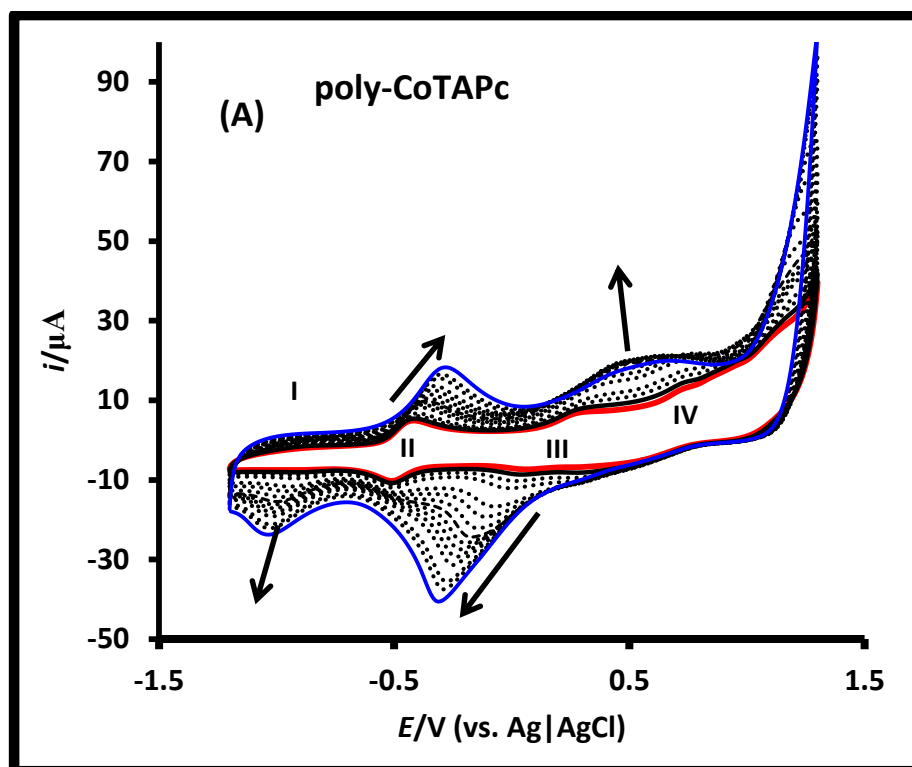
Scheme 4.1. Possible electrooxidative coupling for the preparation of poly-CoPyPc in DMF.

4.1.3.1. Polymerization.

The cyclic voltammetry profiles (Fig. 4.7A-D) for the electrochemical formation of thin films poly-CoTAPc and poly-CoPyPc was achieved through repetitive potential scanning in $1 \times 10^{-3} \text{ mol L}^{-1}$ of their respective monomeric phthalocyanines, in freshly

distilled DMF containing 0.1 M TBABF₄ supporting electrolyte. Polymerization of CoTAPc on bulk carbon electrodes is well known [15,76-78].

Figs. 4.7A and B show the electropolymerization of CoTAPc on GCE and on adsorbed MWCNT, respectively. Fig. 4.7C and D show the electropolymerization of CoPyPc on GCE and on MWCNT-GCE, respectively. During polymerisation process it was observed in all cases that the first scans (red lines) were different from subsequent scans, an indication of polymer formation. Furthermore, subsequent scans exhibited increasing currents, and this confirms the growth and development of better conducting polymeric species on electrode surface.



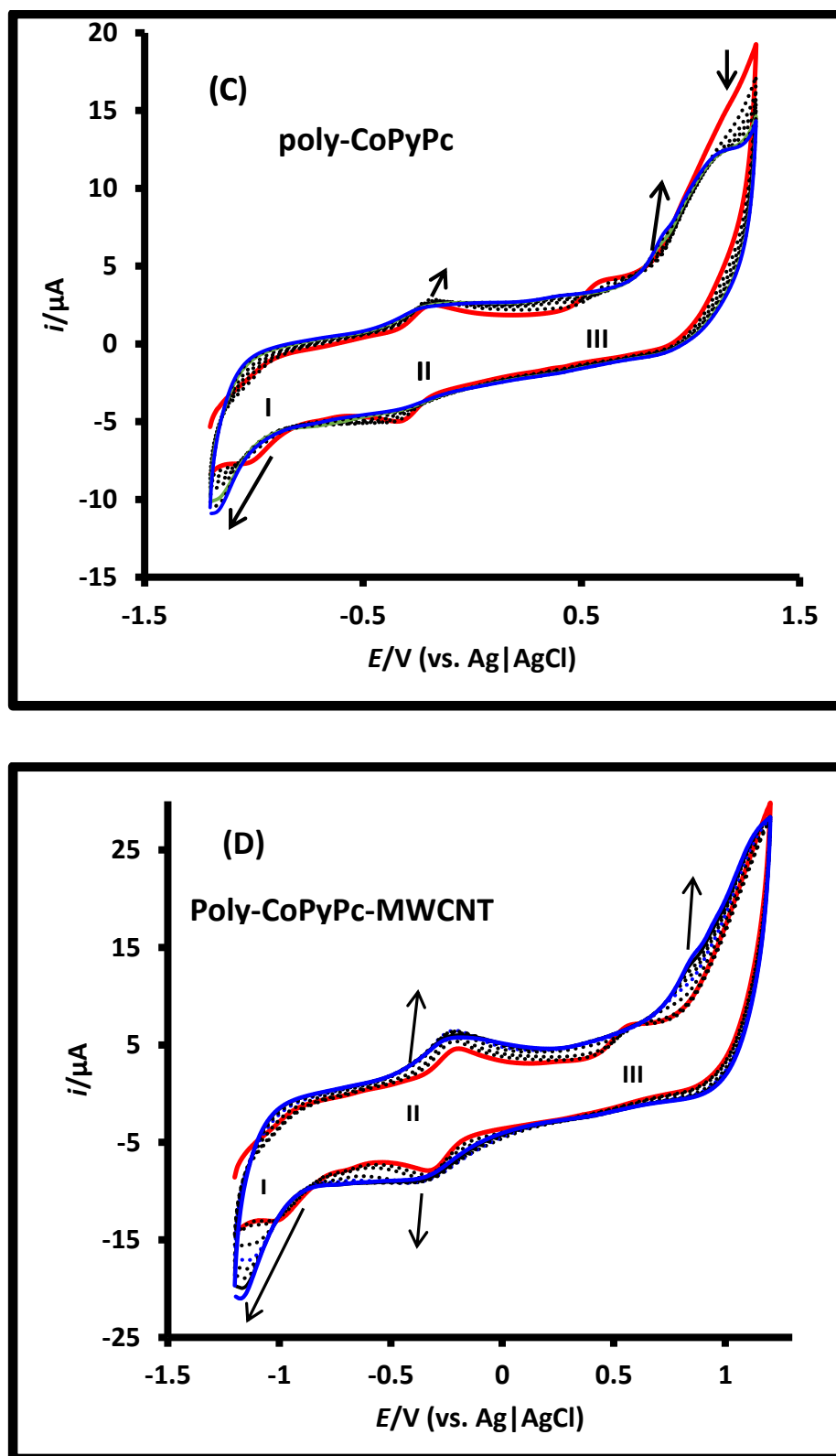


Fig. 4.7. Repetitive cyclic voltammograms of (A,B) 1 mM CoTAPc on GCE (A) and MWCNT-GCE (B); (C,D) 1 mM CoPyPc on GCE (C) and MWCNT-GCE (D); In DMF containing 0.1 M TBABF₄. Scan rate = 100 mV/s.

Figs. 4.8A and B show comparative CVs of the polymeric forms in the presence and absence of MWCNT. Only scans number 8 were plotted for comparison in (Fig. 4.8). Fig. 4.8 shows a remarkable increase in conducting properties when the polymeric forms were formed on MWCNT, hence confirming that MWCNT promote electron transfer. The increase in currents in the presence of MWCNTs, is also evident in Fig. 4.7.

Process II in Fig. 4.7 may be assigned to $\text{Co}^{\text{II/I}}$ redox couple while process III is likely to correspond to $\text{Co}^{\text{III/II}}$ redox couple in comparison with literature [19, 165-167]. Process III is not well resolved as has been observed before [165]. Increasing the number of scan for polymer formation was reported not to improve resolution of these peaks [165]. The peaks near 1 V are associated with the oxidation of the amino group [168]. The rest of the processes are phthalocyanine ring based.

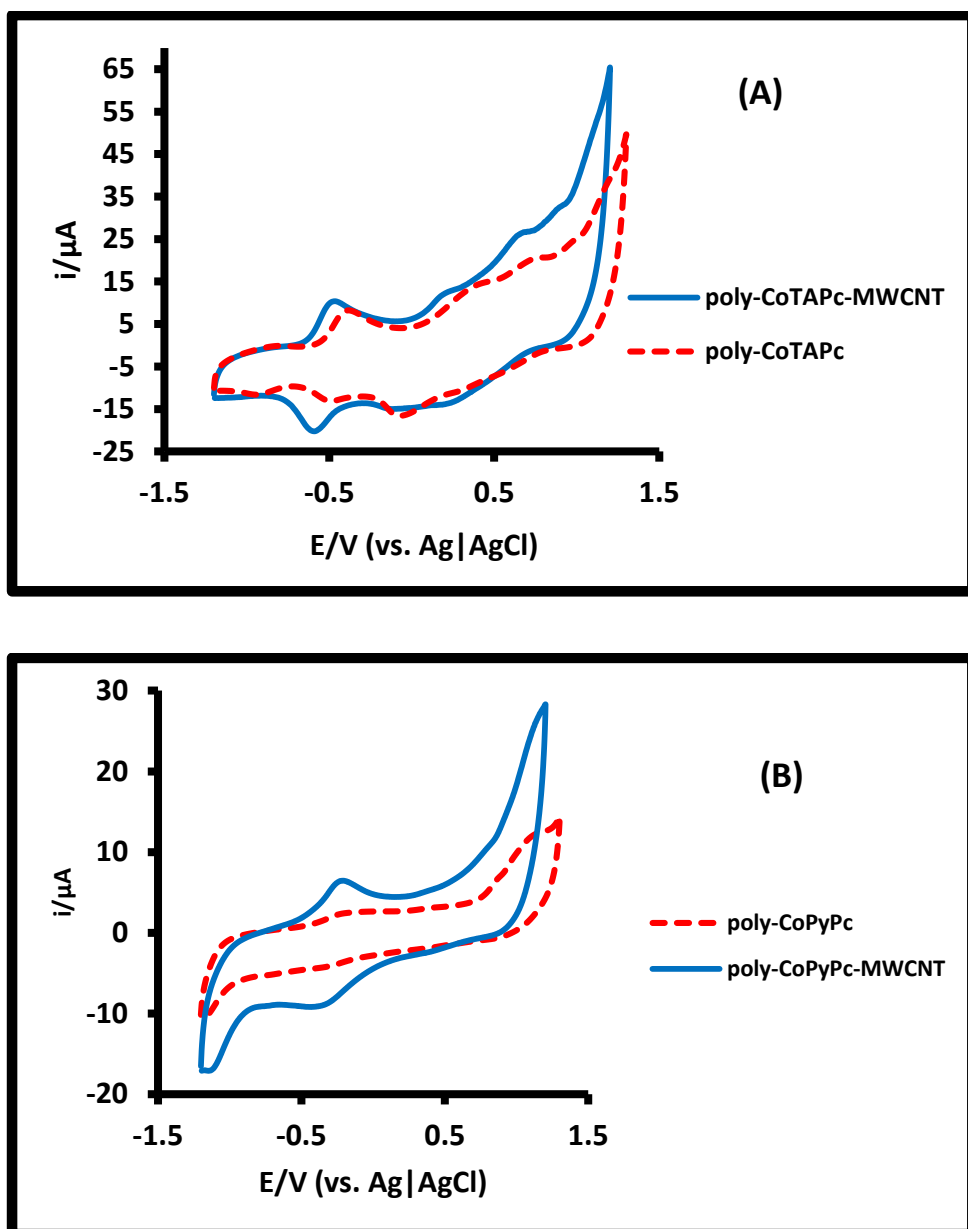


Fig. 4.8. Comparative cyclic voltammograms of the 8th scan during the polymerization of 1 mM (A) CoTAPc and (B) CoPyPc on GCE and MWCNT in DMF containing 0.1 M TBABF_4 . Scan rate = 100 mV/s.

4.1.3.2. Kinetics.

CVs were run for each modified electrode system at varying scan rates in pH 4 buffer system, Fig. 4.9 (using CoPyPc as an example).

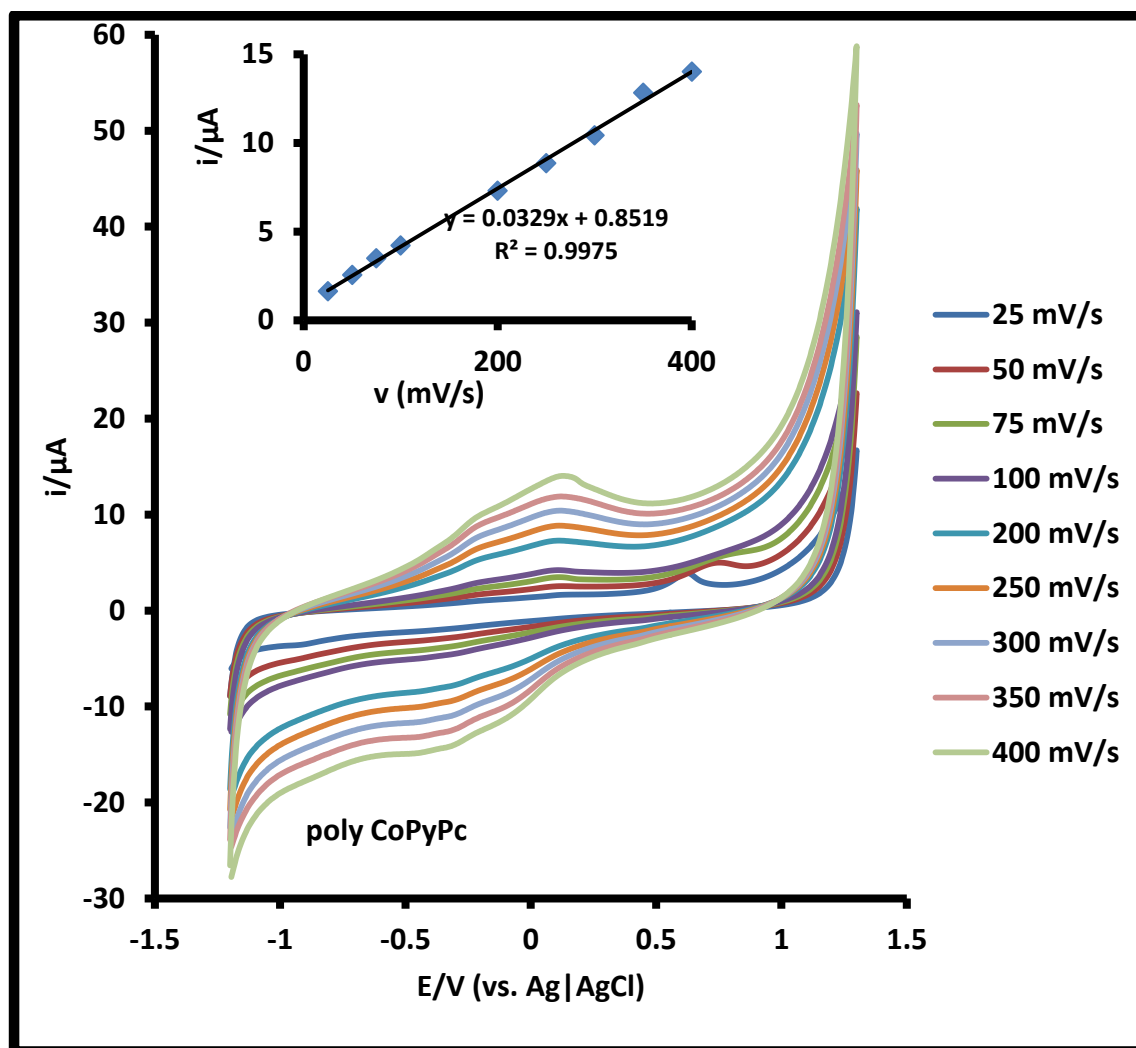


Fig. 4.9. Cyclic voltammograms of poly-CoPyPc thin film on bare GCE in pH 4 buffer solution, (inset = plot of i_p vs. v).

The data obtained Fig.4.9 inset was used to estimate the surface coverages ($\Gamma_{\text{poly-CoPc}}$ or poly-CoPc-MWCNT) using equation (4.1)

$$I_p = \frac{n^2 F^2 \nu A \Gamma_{\text{poly-CoPc/ poly-CoPc-MWCNT}}}{4RT} \quad (4.1)$$

where I_p , n , F , ν , A , and Γ are redox peak current, number of electrons, Faraday's constant, scan rate, electrode surface area (obtained from equation 4.2 below), and surface coverage of the catalyst, respectively. The slope from the plots of I_p vs. ν , Fig.4.9 (inset) was then used to calculate surface coverages. Values are summarised in Table 4.3. The active electrode area of the modified GCE was obtained through the Randles-Sevcik, equation 4.2 [169].

$$i_p = 2.69 \times 10^5 n A C D^{\frac{1}{2}} \nu^{\frac{1}{2}}, \quad [4.2]$$

where i_p = current maximum in amps, A = active electrode area in cm^2 , n = number of electrons transferred in the redox process = 1, C = concentration in $\text{mol}/\text{cm}^3 = 1 \times 10^{-6} \text{ mol}/\text{cm}^3$, D = diffusion coefficient in cm^2/s of the redox system and ν = scan rate in V/s . The $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox system was employed with a diffusion coefficient value of $7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [170].

Table 4.3: Calculated surface coverages for the polymer thin films.

Electrode type	Surface coverage, Γ (mol. cm^{-2})
poly-CoTAPc-GCE	2.69×10^{-9}
poly-CoTAPc-MWCNT-GCE	2.33×10^{-9}
poly-CoPyPc-GCE	3.04×10^{-10}
poly-CoPyPc-MWCNT-GCE	3.49×10^{-10}

The Γ -values for poly-CoTAPc and poly-CoTAPc-MWCNT are higher than for poly-CoPyPc and poly-CoPyPc-MWCNT. This can be attributed to the different functionalities between the substituent groups which influence different pathways for polymer formation. However, there was a small difference in Γ -values between poly-MPcs and their respective nanocomposites (poly-MPc-MWCNT). This indicates that the MWCNT have no strong influence on polymer formation but only enhance electron transfer of the polymeric MPcs. Γ -values for all the catalysts are greater than $1 \times 10^{-10} \text{ mol.cm}^{-2}$ which is expected for a monolayer of a Pc molecule lying flat on the electrode surface [171,172]. This might be expected due to polymer layer formation on a MWCNT layer. Furthermore, multiple formation of polymer layers can also result on both MWCNT and GCE surface due to repetitive scanning during electropolymerisation.

4.1.3.3. Scanning electron microscopy (SEM) studies.

Some structural changes of the MWCNT were observed after polymerisation (Fig. 4.10). The nanotubes were observed to be thicker after polymerisation within same magnification range, an indication that a polymer film was formed around the nanotubes. Also sheet-like structures were observed after polymerisation within the nanocomposite (Fig. 4.10B), which is further confirmation of successful polymerization to form the polymer nanocomposite. This sheet-like structure also confirms the proposed mechanism in which both straight and side polymer chains are produced during repetitive cyclisation of the monomer solution at a MWCNT modified GCE surface.

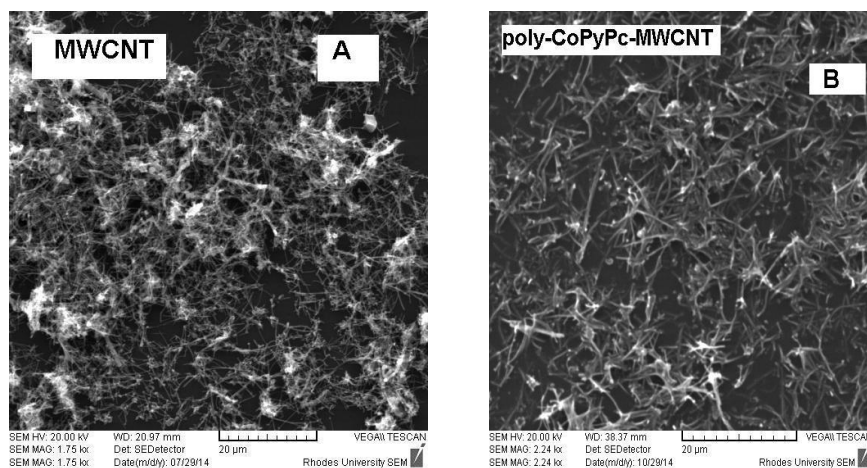


Fig. 4.10. SEM images (on glassy carbon plates) of MWCNT before (A) and after polymerisation with CoPyPc (B).

4.1.3.4. XPS characterization of poly-CoTAPc and poly-CoPyPc.

XPS analysis was used to check if sulphur of CoPyPc is involved in the polymerization process to form poly-CoPyPc. Figs. 4.11A and B show the wide scan XPS for poly-CoTAPc and poly-CoPyPc, respectively. These surveys were deconvoluted at high resolution to get more information for different functionalities/chemical environments of the polymers. Fig. 4.11C shows the deconvoluted spectrum of S 2p_{3/2}. Only one peak was observed at 163.8 eV. One S 2p peak has been reported before [173]. This has been assigned to sulphur in a chemical environment of C-S-C, according to the NIST Standard Reference Database [174,175]. This agrees well with the structure of CoPyPc shown in Scheme 4.1, in which the sulphur is the bridging atom between the MPc ring and the substituent, and not with a neighbouring MPc monomer ring. The proposed polymer is shown in Scheme 4.1.

The N 1s spectrum for poly-CoPyPc (Fig. 4.11D) shows three main peaks after deconvolution, implying the existence of nitrogen in three different chemical environments in the polymer. These can be assigned to C-N=C/ C-N-C (398.8 eV) nitrogens mainly from MPc rings and the other nitrogens involved in the polymerization process as the interconnectors between monomeric MPcs units as depicted in Scheme 4.1. Peaks at 400.4 eV and 402.3 eV can be assigned to -N⁺H and =N⁺H, respectively. These are oxidized amine groups which have not taken part in polymer formation, and the presence of the positive charge shifts their binding energies to more positive values than -NH₂ (~399.1 eV [176]). Similar spectra were obtained for poly-CoTAPc (Fig. 4.11E) after deconvolution, indicating same electropolymerisation mechanism for the two polymeric forms. This is further evidence supporting that sulphur is not participating in the growth of conducting polymer films, but N is involved.

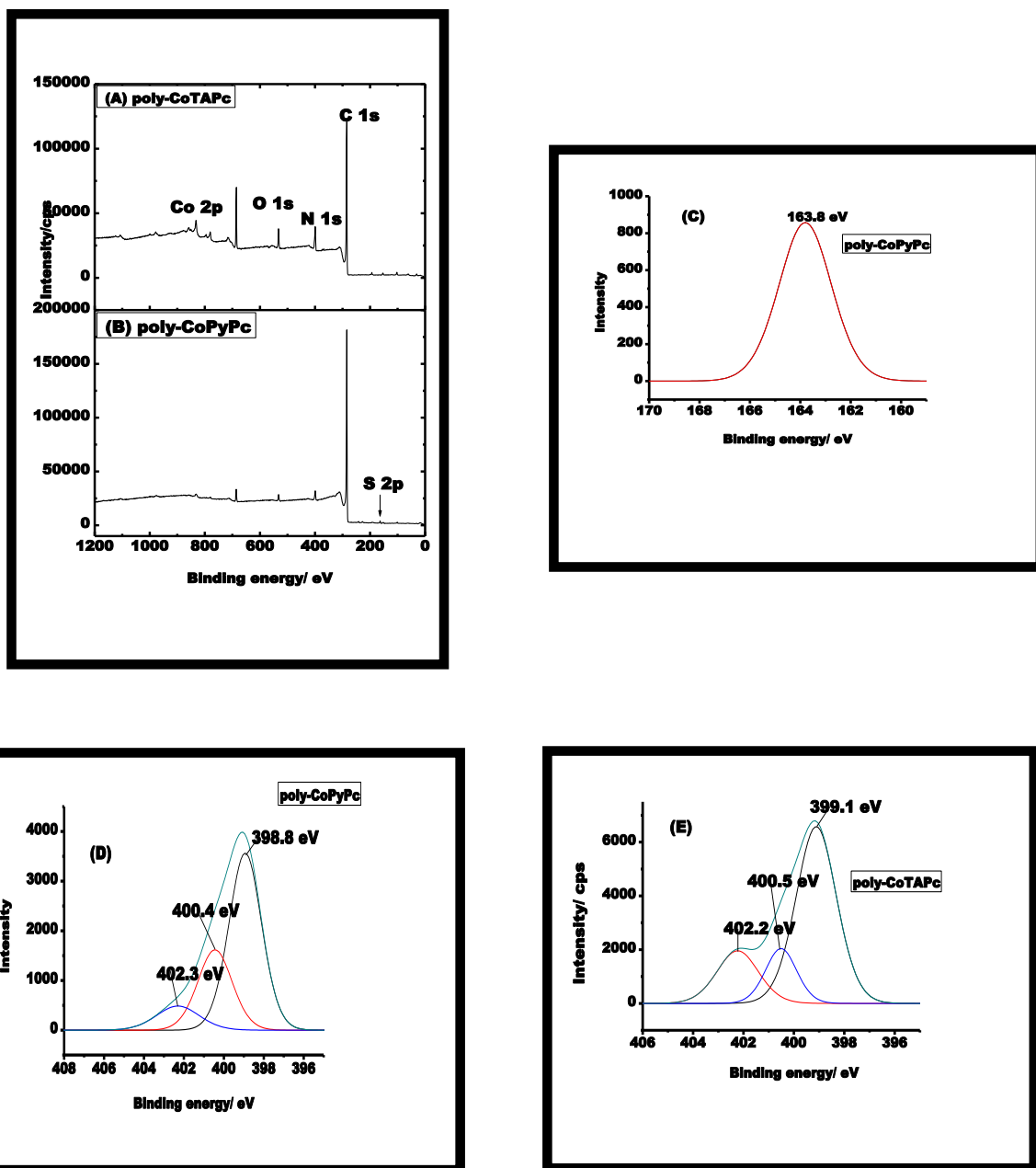
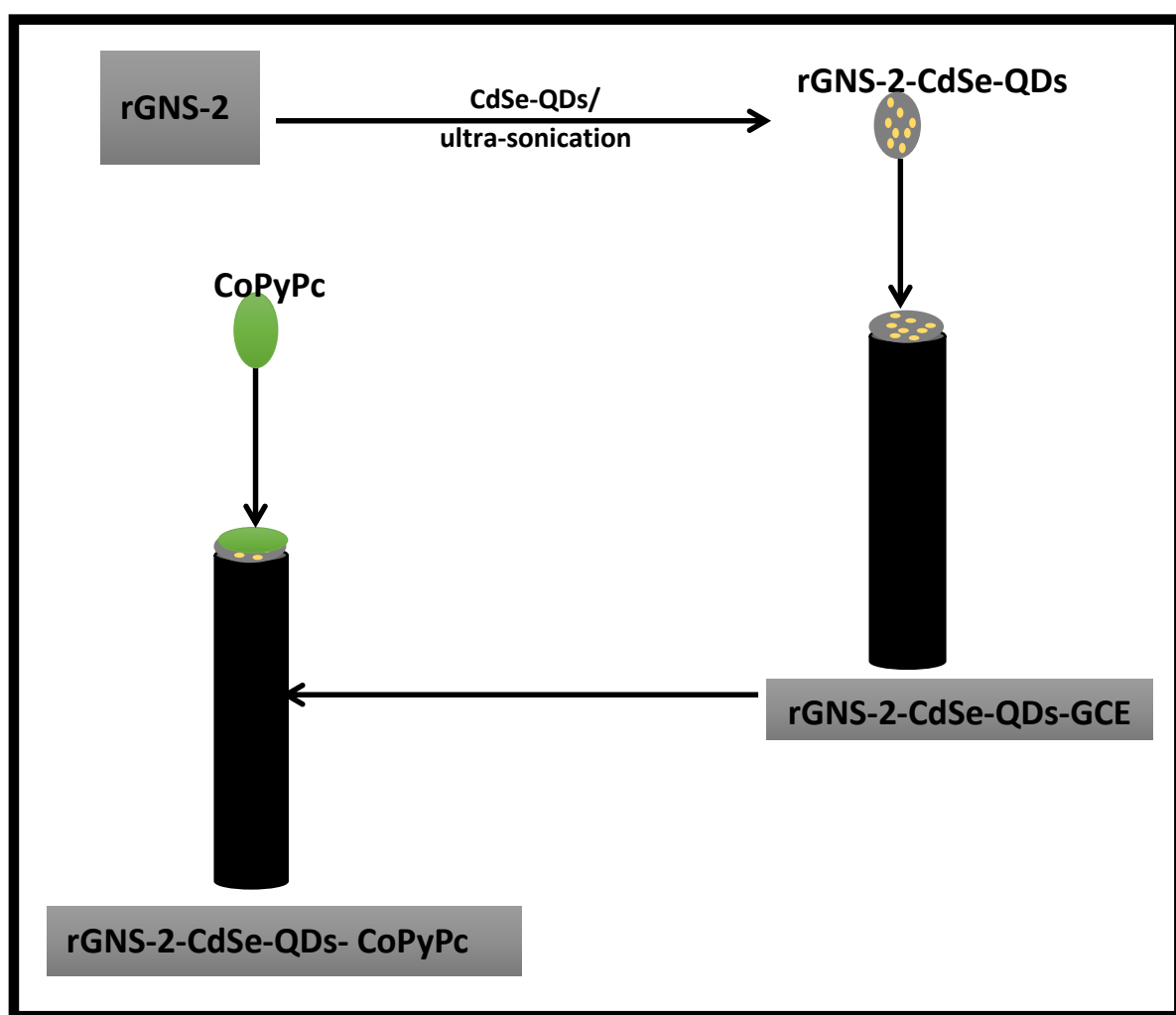


Fig. 4.11. Wide scan XPS spectra for poly-CoTAPc (A), poly-CoPyPc (B), High resolution deconvoluted XPS peaks for S 2p (C) and N 1s for poly-CoPyPc (D), and N 1s for poly-CoTAPc (E). All on MWCNT modified glassy carbon plates.

4.2. CoPyPc based nanocomposites.

4.2.1. Cyclic voltammetry (rGNS-2-QDs based electrodes).

Electrodes modified in a sequential manner in this section, and this is stated in tables and figure captions but not in text. Scheme 4.2 shows electrode modification using combinations of QDs, rGNS-2, and CoPyPc.



Scheme 4.2. Electrode modification using combinations of CdSe-QDs, rGNS-2 and CoPyPc.

Cyclic voltammetry studies of these different electrodes in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl are shown in Fig. 4.12. In relation to the peak potential separation, the following order of electron transfer properties was obtained; CdSe-QDs (0.27 V) < CoPyPc (0.15 V) $\approx$ rGNS-2 (0.15 V) < rGNS-2-CdSe-QDs (0.14 V) < CdSe-QDs-CoPyPc (0.13 V) < CoPyPc-rGNS-2 (0.12 V) < CoPyPc-rGNS-2-CdSe-QDs (0.10 V) < bare GCE (0.08 V), Table 4.4.

In the nanocomposites, CdSe-QDs act as the spacers for individual graphene sheets to prevent restacking, and rGNS provide a catalytic platform for CoPyPc and enhancing electron transfer properties at the GCE interface. The different nanocomposite combinations show that CdSe-QDs intercalated rGNS is a good platform or support for enhancing electron transfer as judged by the lowest ΔE values, Table 4.4.

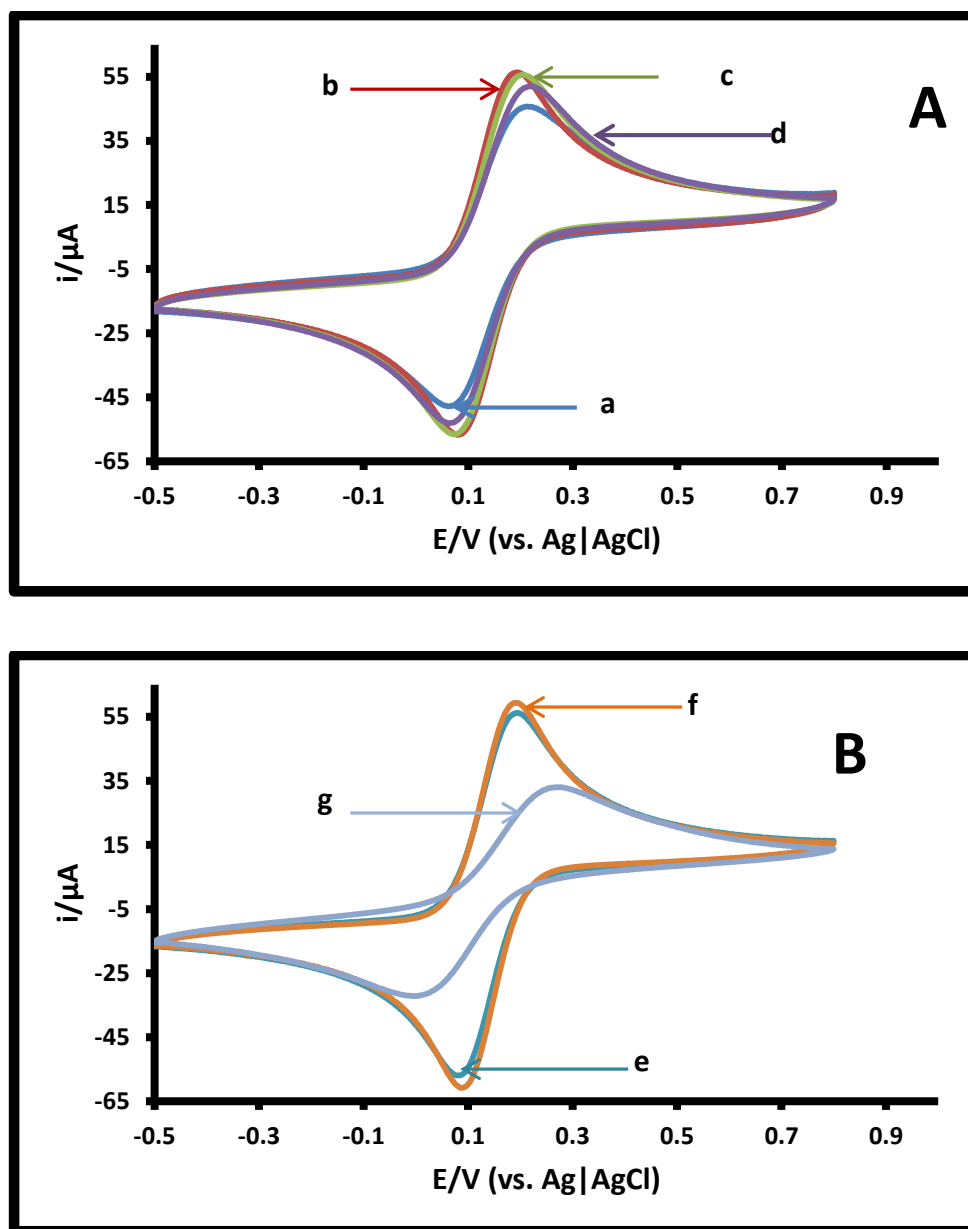


Fig. 4.12. Cyclic Voltammograms of modified electrodes in 2 mM $\text{Fe(CN)}_6^{3-/4-}$ (A): rGNS-CdSe-QDs (mixed) (a), CoPyPc-rGNS-2 (sequential) (b), CoPyPc-CdSe-QDs (sequential) (c), rGNS-2 (d), (B): CoPyPc (e), CoPyPc-rGNS-2-CdSe-QDs (sequential) (f), CdSe-QDs (g). Supporting electrolyte = 0.1 M KCl, Scan rate = 100 mV/s.

Table 4.4. Peak potential separation for different electrodes in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl electrolyte.

Electrodes	ΔE_p / V for $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl
CdSe-QDs	0.27
rGNS-2	0.15
CoPyPc	0.15
CoPyPc-rGNS-2 (sequential)	0.12
rGNS-CdSe-QDs (mixed)	0.14
CoPyPc-CdSe-QDs (sequential)	0.13
CoPyPc-rGNS-2-CdSe-QDs (sequential)	0.10
Iodine doped CoPyPc-MWCNTs (sequential)	0.10
Iodine doped-CoPyPc	0.11
CoPyPc-MWCNTs (sequential)	0.11
MWCNTs (not functionalized)	0.12
MWCNT-COOH	0.14
Bare GCE	0.08
CoPyPc-MWCNTs linked [#]	0.11
CoPyPc-MWCNT-COOH mixed [#]	0.13

[#]MWCNTs used were acid functionalized.

4.2.2. CoPyPc-MWCNT nanocomposites.

4.2.2.1. Cyclic voltammetry.

The electrochemical performance of the bare and modified electrocatalytic surfaces was first established through their electrocatalytic activity in $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe, Fig. 4.13.

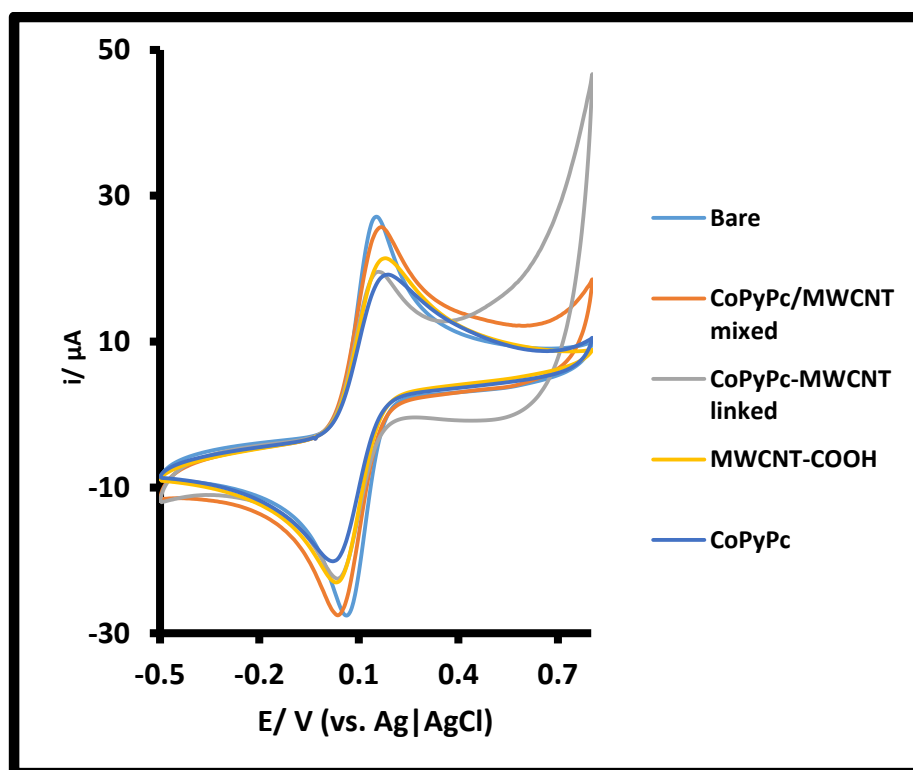


Fig. 4.13. Cyclic Voltammograms of modified electrodes in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ and 0.1 M KCl electrolyte. Scan rate = 100 mV/s.

The peak potential separations (ΔE) for each CV (Fig.4.13) were found to increase in the following order; bare (0.08 V), CoPyPc-MWCNT linked (0.11 mV), CoPyPc-MWCNT mixed (0.13 V), MWCNT-COOH (0.14 V), and CoPyPc (0.15 V), Table 4.4. This trend clearly demonstrates that nanocomposite platforms have better electron transfer properties than individual catalysts. Furthermore, the covalently linked nanocomposite has a ΔE value lower than the mixed nanocomposite, predicting that

it is likely to give better performance in electrocatalysis applications. The behavior of these surfaces under hydrodynamic conditions was further probed using RDE voltammetry as discussed in the next section.

4.2.2.2. RDE.

RDE voltammetry studies of these different electrodes in 1 mM Fe(CN)₆^{3-/4-} in the presence of 0.1 M KCl electrolyte are shown in Fig. 4.14A-D. RDE experiments were not done for other electrodes above and are done here as examples.

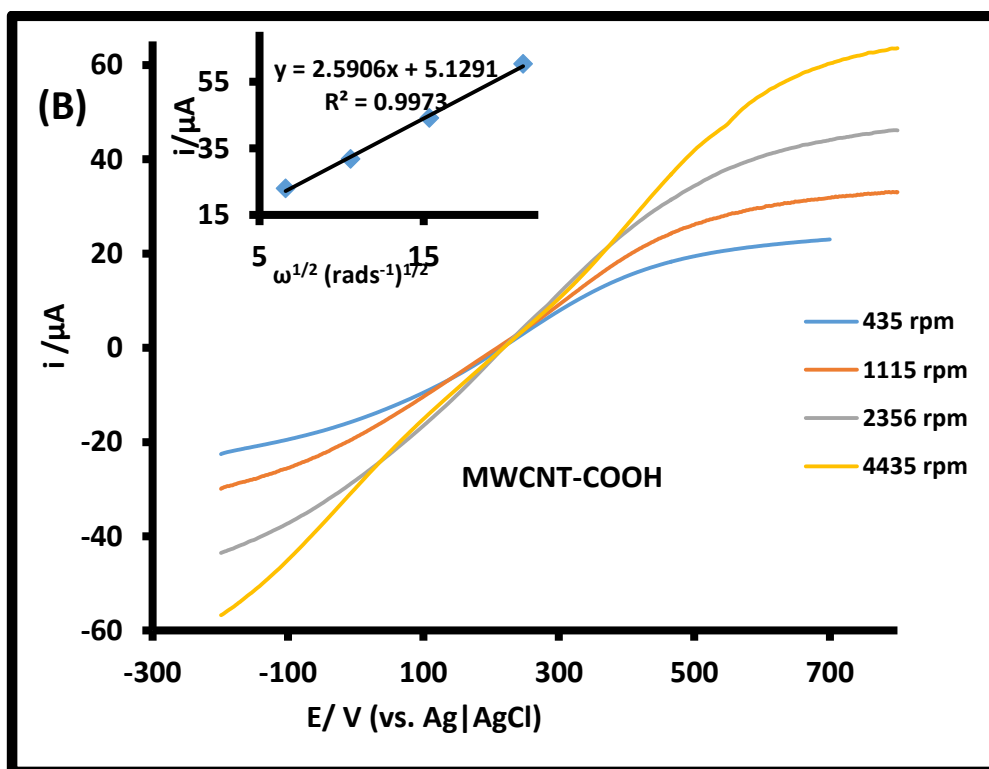
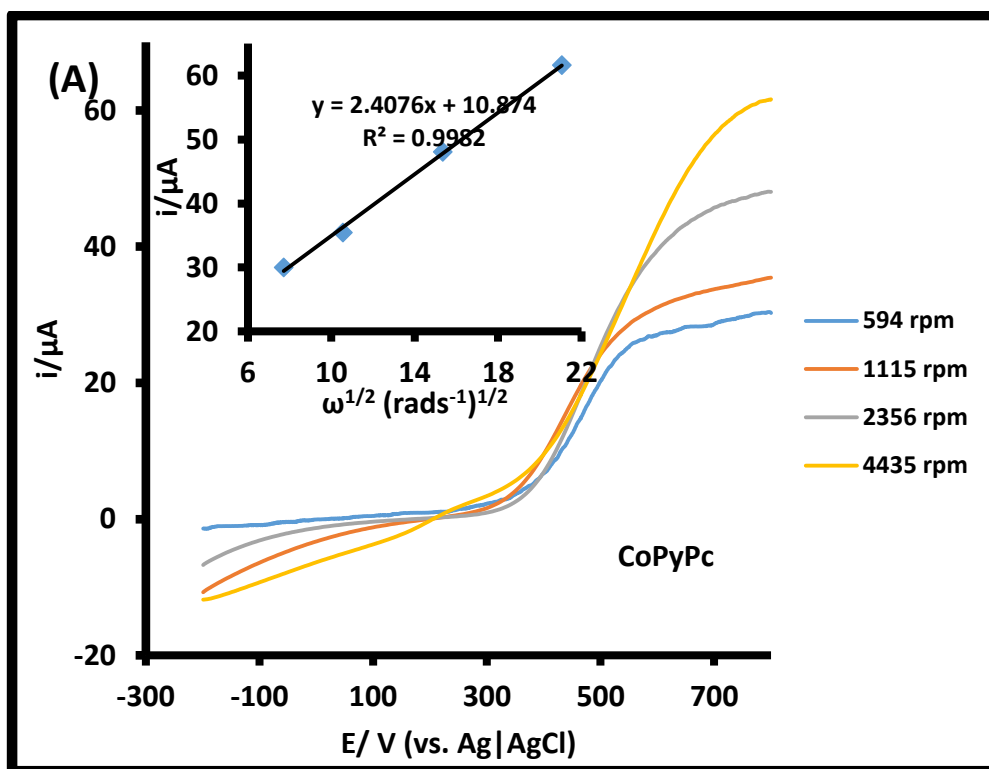
The electrocatalytic performance of the nanocomposites was compared in relation to the kinetic rate constants using maximum limiting currents at increasing rotational speed according to the Koutecky-Levich equation 4.3 [169].

$$\frac{1}{i} = \frac{1}{nFAkC} + \frac{1}{0.62nFA\nu^{\frac{-1}{6}}D^{\frac{2}{3}}\omega^{\frac{1}{2}}C} \quad (4.3)$$

where n = number of electrons, A = effective surface area of the electrode in cm², D = diffusion coefficient in cm² s⁻¹, ν = kinematic viscosity, k= reaction rate constant in cm s⁻¹, and C = bulk concentration of analyte in mol cm⁻³. The Levich plots (i vs. ω^{1/2}) (Fig. 4.14A-D insets) were observed to be linear for all the individual nanomaterials and nanocomposites indicating a diffusion controlled electrocatalytic activity as predicted by the Levich equation 4.4 [169];

$$i_L = 0.62nFAD^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{\frac{-1}{6}}C \quad (4.4)$$

The kinetic rate constants (k) at the bare and modified electrode surfaces in 1 mM Fe(CN)₆^{3-/4-} redox probe were obtained by the Koutecky-Levich plots from equation 4.3, Table 4.5.



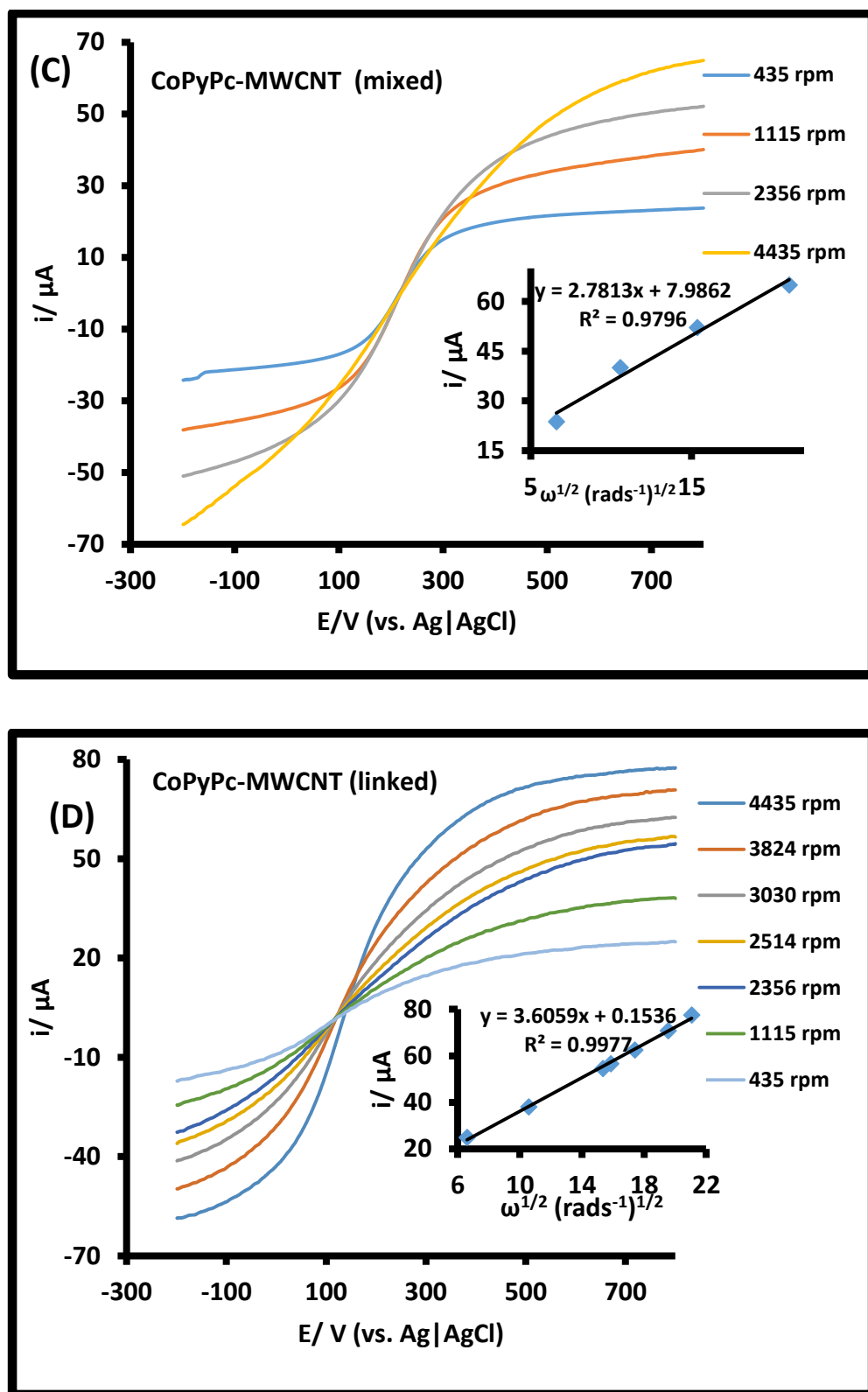


Fig. 4.14. RDE voltammograms of 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ using (A) CoPyPc, (B) MWCNT-COOH, (C) CoPyPc-MWCNTs (mixed) and (D) CoPyPc-MWCNT (linked). Electrolyte = 0.1 M KCl electrolyte; Scan rate = 10 mV/s; Inset = Levich plot.

Table 4.5: A summary of kinetic parameters of bare and different films on electrode surface obtained in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ by the Koutecky-Levich plots.

Electrode	k (cm s^{-1})	Slope
Bare	5.03×10^{-2}	0.293
CoPyPc	2.12×10^{-2}	0.212
MWCNT-COOH	2.56×10^{-2}	0.254
CoPyPc-MWCNT (mixed)	6.35×10^{-2}	0.257
CoPyPc-MWCNT (linked)	1.46×10^{-1}	0.261

The rate constant values were obtained from the intercepts of the plots in Fig. 4.15, equation 4.3. The following order in kinetic rate constants was obtained from these studies; $\text{CoPyPc} < \text{MWCNT} < \text{Bare} < \text{CoPyPc-MWCNT (mixed)} < \text{CoPyPc-MWCNT (linked)}$. Thus, the bare electrode performed better than CoPyPc or MWCNTs alone. This order reflects the significance of nanocomposites in designing catalytic platforms, especially the enhancement of electrocatalytic performance of MPc complex in the presence of MWCNT.

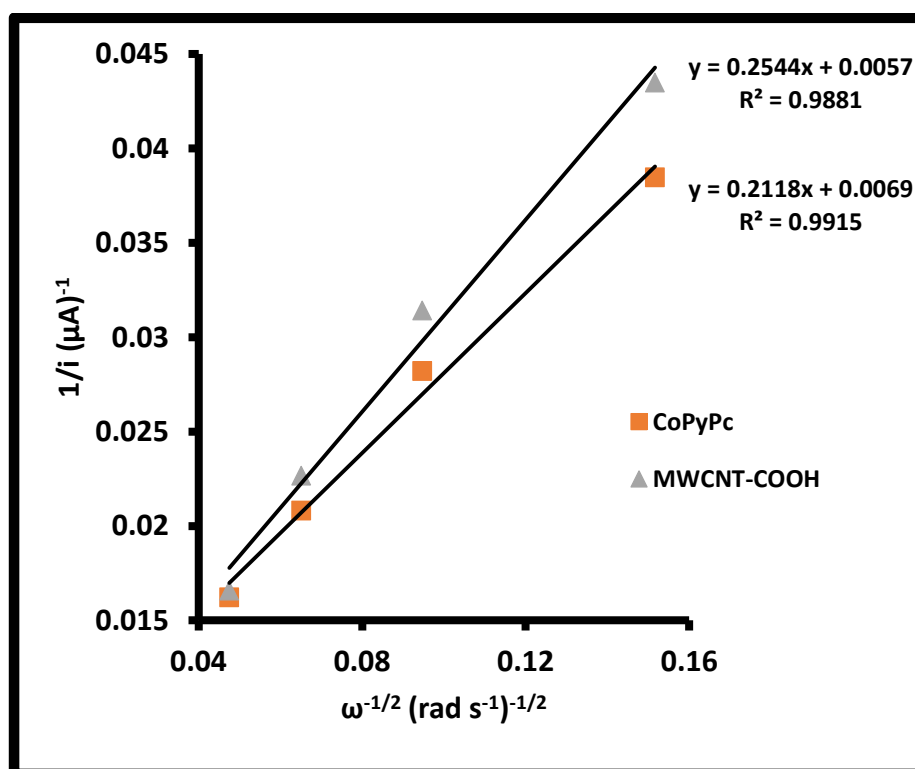
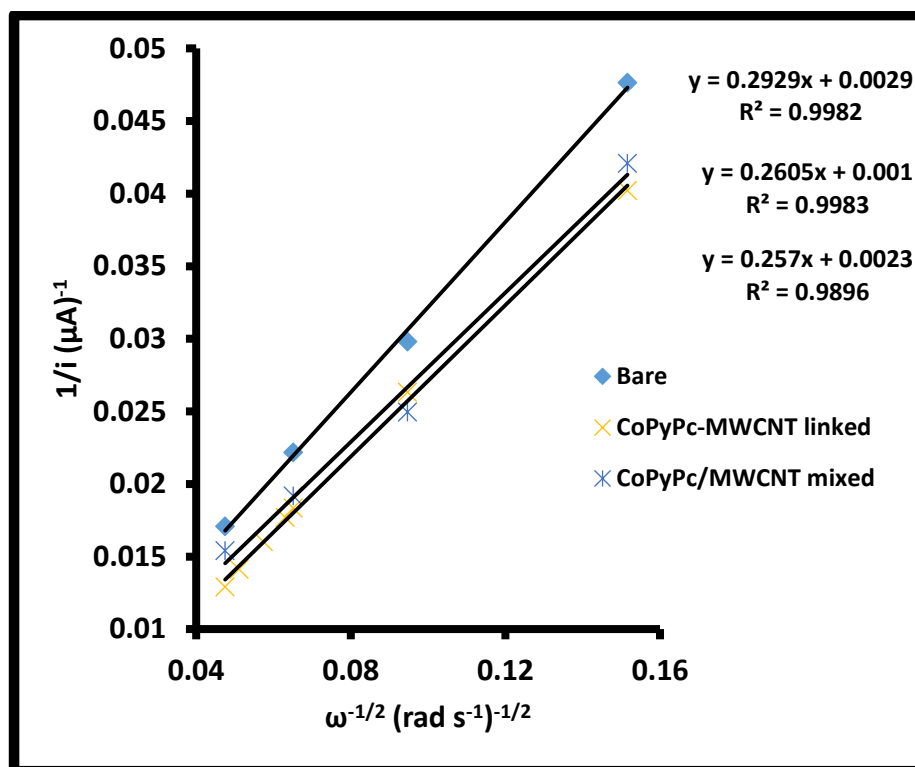


Fig. 4.15. Koutecky-Levich plots in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ using the bare and modified GCE surfaces.

The kinetic data shows that there is better enhancement of electron transfer properties when the nanocomposite is made from covalently linked MPc and MWCNT than when the two components are simply mixed. Covalently linked nanocomposites are also partially π - π stacked onto MWCNT as discussed above, resulting improved interaction, hence improved kinetic data. This gives the observed better/faster electron transfer properties for the linked nanocomposite electrocatalyst. Parallel lines of the plots of i^{-1} vs. $\omega^{-1/2}$ (where i is the current obtained from the rising part of the RDE voltammograms for each rotational speed, figure not shown) were used to confirm first order reaction with respect to the redox probe. After evaluation of the behaviour of these catalysts in $\text{Fe}(\text{CN})_6^{3-/4-}$, practical application was probed for oxidation of a thiol (l-cysteine) as a test analyte in the next chapter.

4.2.3. Iodine doped CoPyPc-MWCNT nanocomposites.

4.2.3.1. SEM.

The SEM images (Fig. 4.16) also show some structural differences on the MWCNT before and after adding the iodine doped CoPyPc. The images show an even surface distribution of the MWCNT or iodine doped CoPyPc-MWCNT on the glassy carbon plate but the coverage is not complete. The presence of iodine doped CoPyPc on the SEM of MWCNT is observed by the increase in white spots. Phthalocyanines are known to exhibit metallic behaviour when partially oxidized and adopting a face-to-face stacking [108,109]; hence the iodised CoPyPc-MWCNT nanocomposite shows more reflective surface features on SEM images.

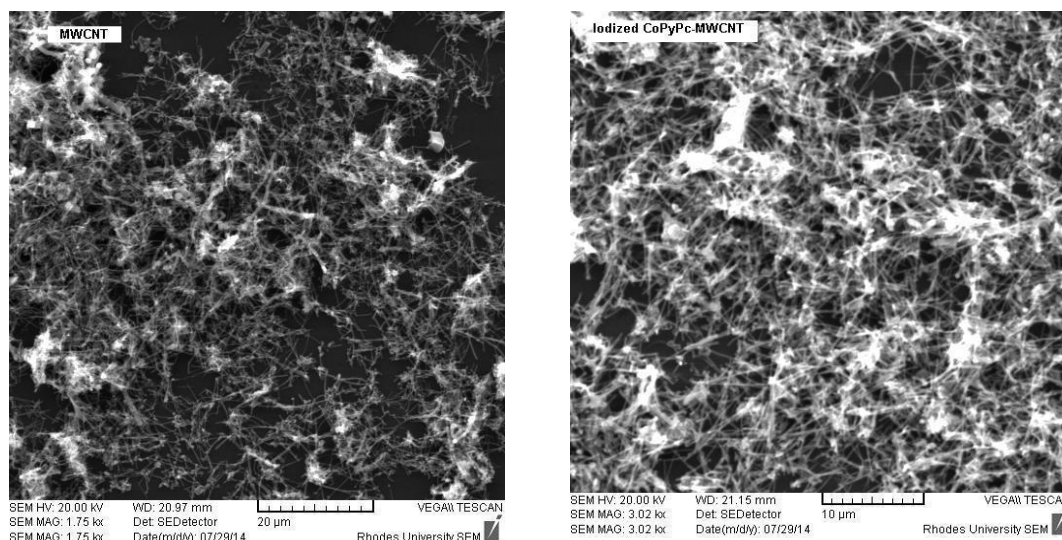


Fig. 4.16. SEM images for MWCNT and iodine doped-CoPyPc-MWCNT on glassy carbon plates.

4.2.3.2. Cyclic Voltammetry.

CV studies of a selection of different electrodes in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl are shown in Fig. 4.17. In relation to the peak potential separation (ΔE_p), the following order in electrocatalytic activity of the Pcs and their nanocomposites on a GCE was obtained: CoPyPc < MWCNT (unfunctionalized) < iodine doped CoPyPc $\approx$ CoPyPc-MWCNT $\approx$ iodine doped CoPyPc-MWCNT, Table 4.4. There was an increase in electron transfer activity of CoPyPc after iodine-doping. The ΔE value decreased by 0.04 V following doping of CoPyPc, Table 4.4. Both CoPyPc and iodised-CoPyPc were sequentially adsorbed onto MWCNT, with further enhancement of electron transfer properties, Table 4.4.

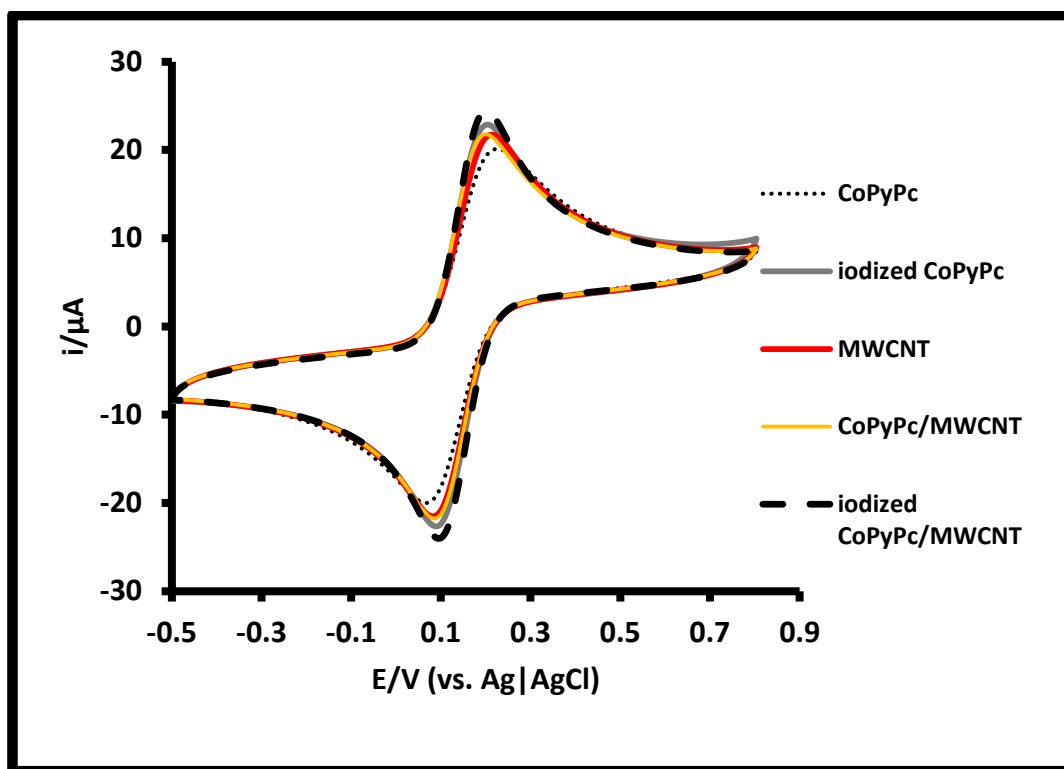


Fig. 4.17. Cyclic Voltammograms of modified electrodes GCE in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$. Supporting electrolyte = 0.1 M KCl, Scan rate = 100 mV/s.

The different nanocomposite combinations reveal that iodine doping as well as the adsorption of the doped phthalocyanine on MWCNT enhances electron transfer significantly. The adsorption of CoPyPc onto MWCNT will occur through π - π interaction [177] between the two due to the existence of extended conjugated systems in both CoPyPc and MWCNT.

4.2.3.3. EIS.

EIS was used to probe into the electrochemical reaction taking place at the electrode/electrolyte interface. The EIS Bode spectra (Fig. 4.18A) show that none of the different electrode surfaces exhibit behaviour typical of a thin passive film since $\theta < 90^\circ$ i.e. no capacitive or near capacitive responses were observed [178].

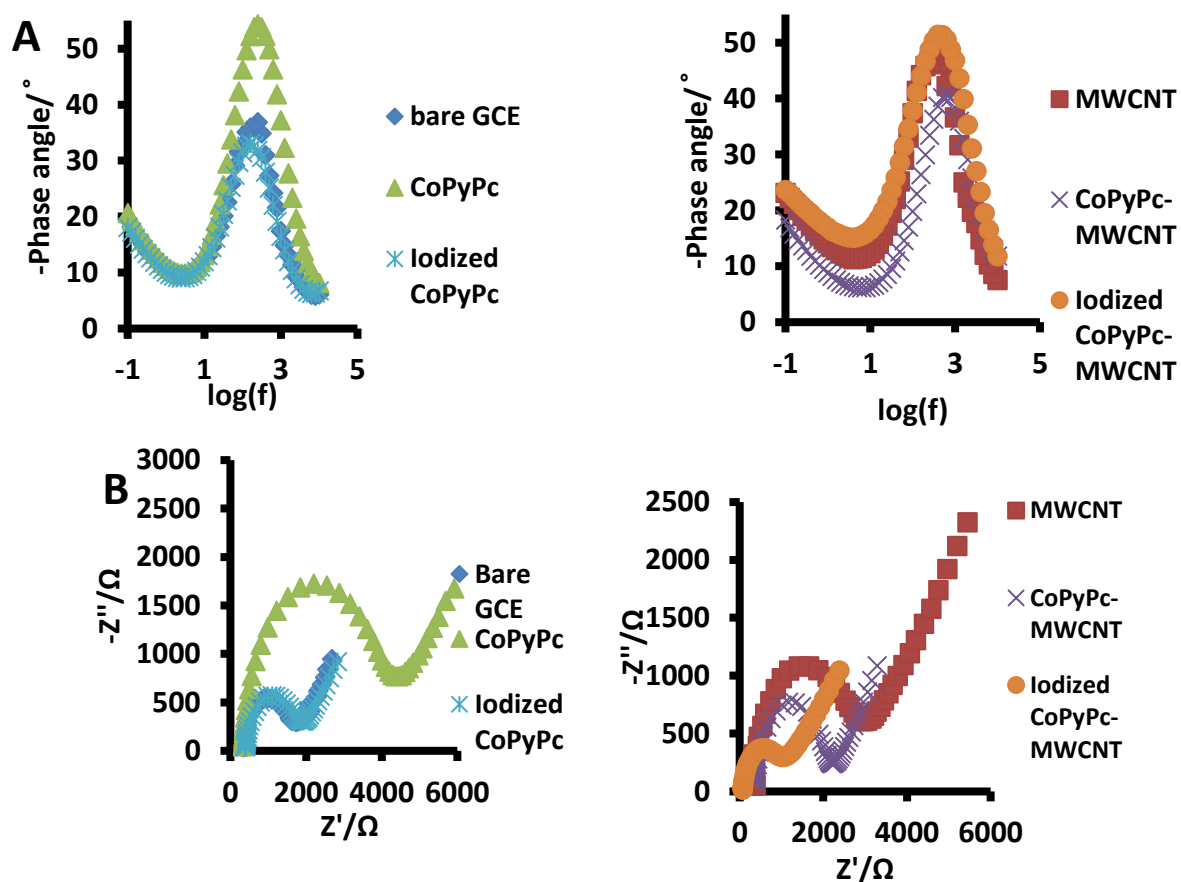


Fig. 4.18. Bode (A) and Nyquist (B) plots obtained using the bare and modified electrodes in air saturated 0.5 M NaOH.

As illustrated by the Bode plots, phase angles are well below -90° and do not spread over a wide frequency range. The Warburg impedance exhibits a phase angle near 45° . The Bode plots confirm the structural differences between the modified and the bare GCE. This is also further confirmed by n -values which are all below a value of 1, Table 4.6, for pure capacitive behaviour. However, the phase angles and n -values are not the same for all surfaces. This implies that the thin films have different electron transfer properties.

As stated earlier, the Nyquist plot (Fig.4.18B) is divided into two frequency regions, the kinetically controlled (high frequency) region where the semi-circle is observed and the diffusion controlled (low frequency) region where the Warburg line is observed. Doping the phthalocyanine resulted in decrease in R_{ct} values from 3.76 k Ω for CoPyPc to 1.42 k Ω for iodine doped CoPyPc, Table 4.6. The R_{ct} values for iodine doped CoPyPc further decreased in the presence of MWCNTs from 1.42 k Ω (for iodine doped CoPyPc) to 0.96 k Ω (iodine doped CoPyPc-MWCNT), Table 4.6. The order of efficiency in electron transfer as deduced from R_{ct} is as follows: iodine doped-CoPyPc-MWCNT > bare GCE > iodine doped-CoPyPc > MWCNT-CoPyPc > MWCNT > CoPyPc. The apparent rate transfer constant (k_{app}) was calculated using Equation 4.5 [179].

$$k_{app} = \frac{RT}{F^2 A R_{ct} C} \quad (4.5)$$

where, $C = [\text{Fe}(\text{CN})_6^{4-/3-}] = 1 \times 10^{-6} \text{ mol cm}^{-3}$, A = electrode surface area in cm^2 (obtained using $\text{Fe}(\text{CN})_6^{4-/3-}$ and eq. 4.2), R_{ct} = resistance to charge transfer obtained from the Nyquist plot (Fig. 4.18B) and R , T , and F take their usual scientific meaning.

Table 4.6: A summary of EIS data for the different surfaces in 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ redox probe in 0.1 M KCl supporting electrolyte.

Electrode surface	R_{ct} ($k\Omega$) ^a	n^a	$k_{app}/\text{cm s}^{-1}$
Iodine doped-CoPyPc-MWCNT-GCE (sequential)	0.96 (1.93%)	0.84 (1.28 %)	3.89×10^{-3}
Iodine doped -CoPyPc-GCE	1.42 (1.07%)	0.85 (0.97 %)	2.64×10^{-3}
CoPyPc-MWCNT-GCE (sequential)	1.79 (0.50%)	0.89 (0.59 %)	2.10×10^{-3}
CoPyPc-GCE	3.76 (0.58%)	0.94 (0.39 %)	9.97×10^{-4}
MWCNT-GCE	2.50 (1.78%)	0.91 (1.29 %)	1.50×10^{-3}
Bare GCE	1.32 (2.57%)	0.87 (0.97 %)	2.84×10^{-3}

^aValues in brackets are established percentage errors for the fit.

These values clearly demonstrate the effect of two processes involved in the fabrication of a catalytic nanocomposite i.e. (i) doping a new cobalt phthalocyanine with iodine, and (ii) and adsorbing the iodine-doped cobalt phthalocyanine on MWCNT for electrocatalysis. The order of k_{app} values is as follows: iodine doped-CoPyPc-MWCNT > bare GCE > iodine doped CoPyPc > CoPyPc-MWCNT > MWCNT > CoPyPc. This trend is a clear indication that a doped hybrid nanocomposite is a better platform for catalysis and can be used as a mediator for electron/charge transfer between analytes and the electrode surface. These surfaces have been further probed for their ORR catalytic activity (Chapter 5).

4.3. Conclusion.

GCE were used as platforms for the preparation of modified electrode surfaces. Higher anodic and cathodic peak currents were observed when the drops of carbon materials (MWCNTs or GNS) and MPcs are added separately (sequential)) on glassy carbon electrode than when premixed. It was observed that experiments where MPc was placed on the electrode first followed by the nanomaterials resulted in low catalytic currents relative to when MPc is placed on top. It is against this background that placing MPc on top was preferred in most cases of this study. Peak currents for the nanocomposite modified surfaces are higher than individual components. This proves the significance of nanocomposites in designing catalytic platforms over individual components, especially the enhancement of electrocatalytic performance of MPc complex in the presence of MWCNT or upon iodine doping.

Chapter Five: Electrocatalysis.

This chapter focusses on the application of the different catalytic platforms towards electrooxidation and electroreduction of analytes. L-cysteine (a thiol), paraquat (a herbicide) and the ORR were used as test analytes for the assessment of the catalytic electrooxidation and electroreduction performance of the catalysts.

5.1. L-cysteine.

5.1.1. CoTAPc (mixed/sequential).

5.1.1.1. Cyclic voltammetry.

Fig. 5.1 compares the electrodes for the detection of l-cysteine to check the effect of sequential versus mixed CoTAPc-MWCNT nanocomposites. The bare GCE electrode, Fig. 5.1A(a) does not show any peak in the presence of l-cysteine within the potential range in Fig.5.1, as reported before [120]. Oxidation peaks were observed when using modified GC electrodes in the presence of l-cysteine (in pH 4 buffer). The appearance of the oxidation peaks with the modified GCE relative to the bare electrode confirms electrocatalysis. Fig. 5.1B(i) shows the CV for CoTAPc with a weak $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ couple at ~ 0.3 V and is indicated by a double dashed arrow. This process is known to be irreversible and very difficult to observe for adsorbed CoPc complexes [166,180]. This couple catalyses the oxidation of l-cysteine [120] on CoTAPc alone or in the presence of MWCNTs.

Fig. 5.1A(d) shows larger peak currents for the CoTAPc-MWCNT(sequential) electrode, confirming better electrocatalytic performance towards oxidation of l-cysteine. It has been reported that only external layers of phthalocyanine modified electrodes are catalytically active towards thiols [181] hence very thin films are sufficient for this application.

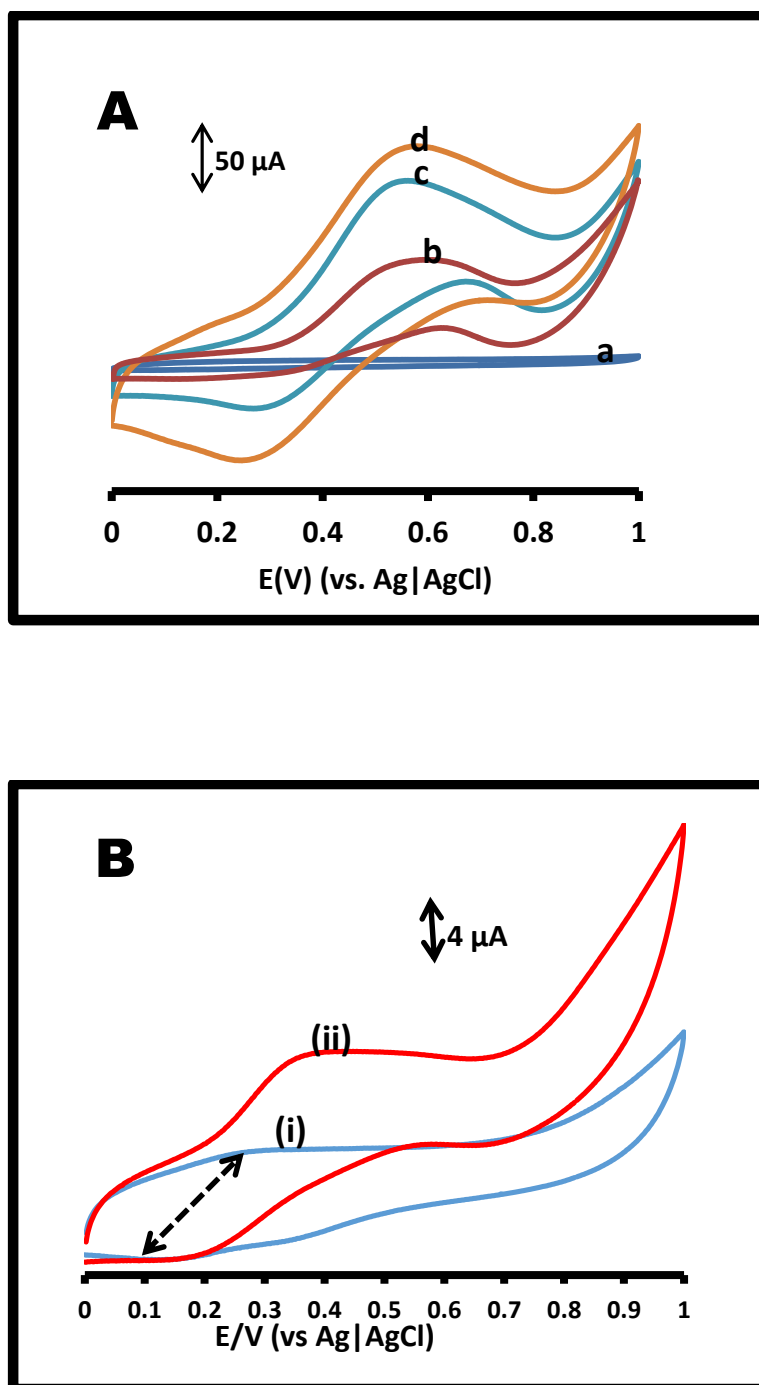


Fig.5.1. (A) Comparative cyclic voltamograms of L-cysteine using bare GCE (a), MWCNTs (b), CoTAPc-MWCNTs (mixed) (c), and CoTAPc-MWCNTs (sequential) (d). (B) CoTAPc modified GCE in pH 4 buffer only in the absence (i) and presence (ii) of 6 mM L-cysteine in pH 4 buffer, scan rate = 100 mV/s.

The dip in the current on the return scan for the oxidation of l-cysteine on modified surfaces (Fig. 5.1A) is typical of electrocatalysis for some analytes such as hydrazine and l-cysteine on CoPc modified electrodes [120,182]. The mechanism for the oxidation of l-cysteine on CoTAPc alone, CoTAPc-MWCNT (sequential) or CoTAPc-MWCNT (mixed) is as proposed before for GCE modified CoPc derivatives at pH 4 [120]. The peak potentials for l-cysteine oxidation on CoTAPc, CoTAPc-MWCNTs (mixed), and CoTAPc-MWCNT (sequential) were found at 0.45 V, 0.60 V, and 0.63 V, respectively, Table 5.1.

Table 5.1. A summary of E_p and sensitivity for the different surfaces using l-cysteine in pH 4 buffer.

Electrode	E_p (L-cysteine oxidation)/ V vs. Ag AgCl	Sensitivity ^a (A/mM)	LOD/ μ M
CoTAPc-MWCNT-GCE (mixed)	0.60	2.0×10^{-5}	0.73
CoTAPc-MWCNT-GCE (sequential)	0.63	1.0×10^{-4} (7.0×10^{-4})	0.42 (0.28)
CoTAPc	0.45	3.0×10^{-6}	1.24
Poly CoTAPc-MWCNT	0.40	27.11×10^{-6}	0.017
Poly CoPyPc-MWCNT	0.55	7.09×10^{-6}	0.036
CoPyPc	0.80	--- ^b	--- ^b
CoPyPc-MWCNTs (linked)	0.50	0.33×10^{-6}	0.296
CoPyPc-MWCNT (mixed)	0.60	--- ^b	--- ^b

^aValues in brackets are when 0.005 mM aliquots of l-cysteine were used. ^bNot calculated because E_p values were inferior to CoPyPc-MWCNT (linked) nanocomposite.

Though the CoTAPc alone had the lowest oxidation potential which is a good feature of electrocatalysis, this is overshadowed by very low anodic peak current intensities. Compare Fig. 5.1A and B current ranges i.e. 50 μ A in Fig. 5.1A (in the presence of MWCNTs) and 4 μ A in Fig. 5.1B (in the absence of MWCNTs). The low anodic peak current intensities imply low sensitivity thereby limiting the suitability of CoTAPc films alone on GCE for fast and ultra-low detection of l-cysteine in aqueous medium. CoTAPc-MWCNT (sequential) has better electrocatalytic properties in terms of i_p value of 4.39×10^{-4} A compared to CoTAPc-MWCNTs (mixed) with a current value of 2.89×10^{-4} A at $E_p = 0.60$ V.

The onset potential was at 0.27 V for CoTAPc-MWCNT (sequential) compared to CoTAPc-MWCNTs (premixed) which was at ≈ 0.36 V, which is again an indication good electrocatalysis for the former. A plot of square root of scan rate versus current gave a linear relationship, Fig. 5.2A, a confirmation that the electrocatalytic oxidation of l-cysteine is diffusion controlled.

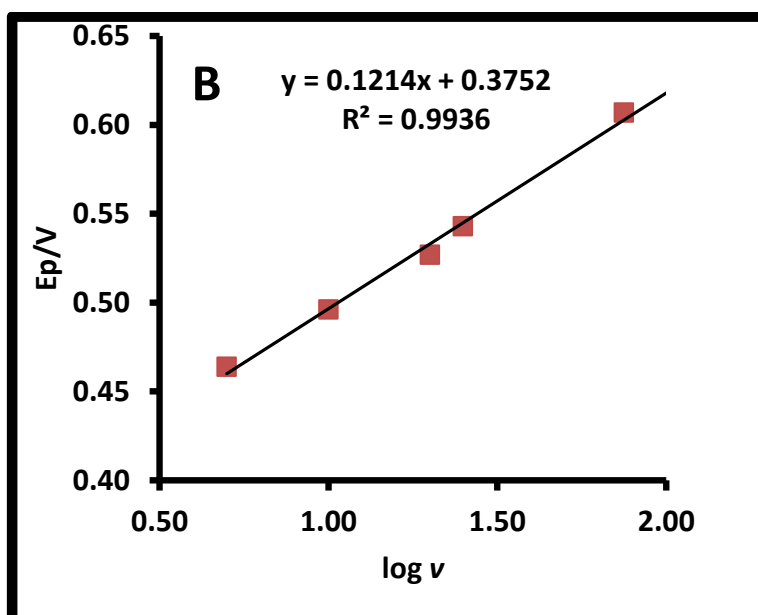
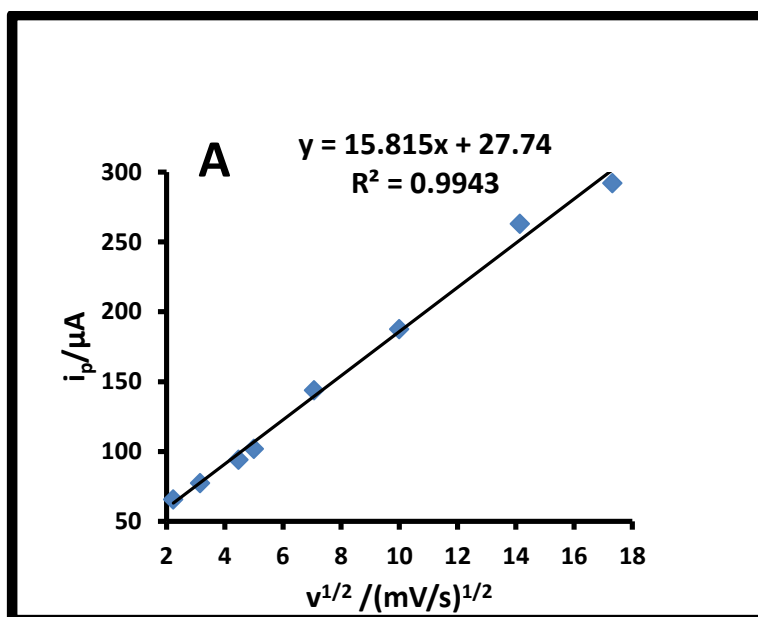
A plot of E_p vs. $\log v$ (Fig. 5.2B) was employed for the determination of a Tafel slope, Eq. (5.1):

$$E_p = \frac{b}{2} \log v + K \quad (5.1)$$

where b = Tafel slope, and v = scan rate.

The gradient of the plot of E_p vs. $\log v$ is equal to $b/2$. In this work the Tafel slope was found to be 243 mV/decade. Tafel slope values within the range 30-120 mV/decade are expected. Tafel slopes larger than 120 mV/decade have been reported [183-185]. A mechanism in which a chemical step is the rate determining has been proposed for processes having high Tafel slopes [185]. Strong l-cysteine-catalyst interactions can also explain high Tafel slopes. Such interactions between CoTAPc and l-cysteine have been reported before using UV-vis spectroscopy [120].

The continuous cyclization of the modified CoTAPc-MWCNT (sequential) in 8 mM l-cysteine was also used to test the stability and resistance to passivation/fouling of the modified surface (Fig. 5.2C). It is clear that the latter cycles give higher peak currents than the initial cycles. This resistance to passivation was further confirmed by chronoamperometric studies discussed in the next section.



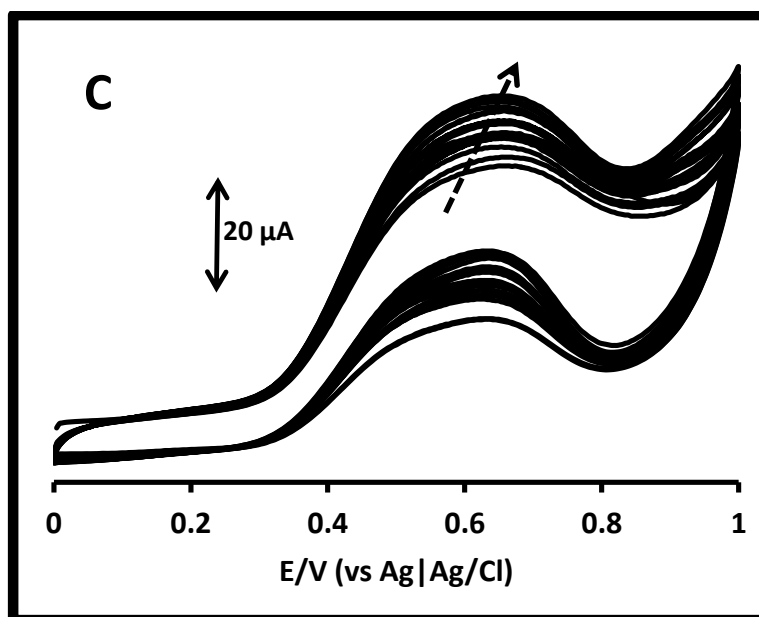


Fig. 5.2. Plots of (A) I_p vs $v^{1/2}$, (B) E_p vs $\log v$ for oxidation of L-cysteine on CoTAPc-MWCNTs (sequential). (C) Continuous cyclisation of in pH 4 buffer in the presence of 8 mM L-cysteine, scan rate = 100 mV/s.

5.1.1.2. Chronoamperometry.

The better sensitivity of the CoTAPc-MWCNT (sequential) was further confirmed by chronoamperometry (CA) studies. The chronoamperometric studies were done to determine parameters such as the catalytic rate constant, limit of detection (LOD), practical limit of quantification (PLOQ) and sensitivity towards the detection of l-cysteine.

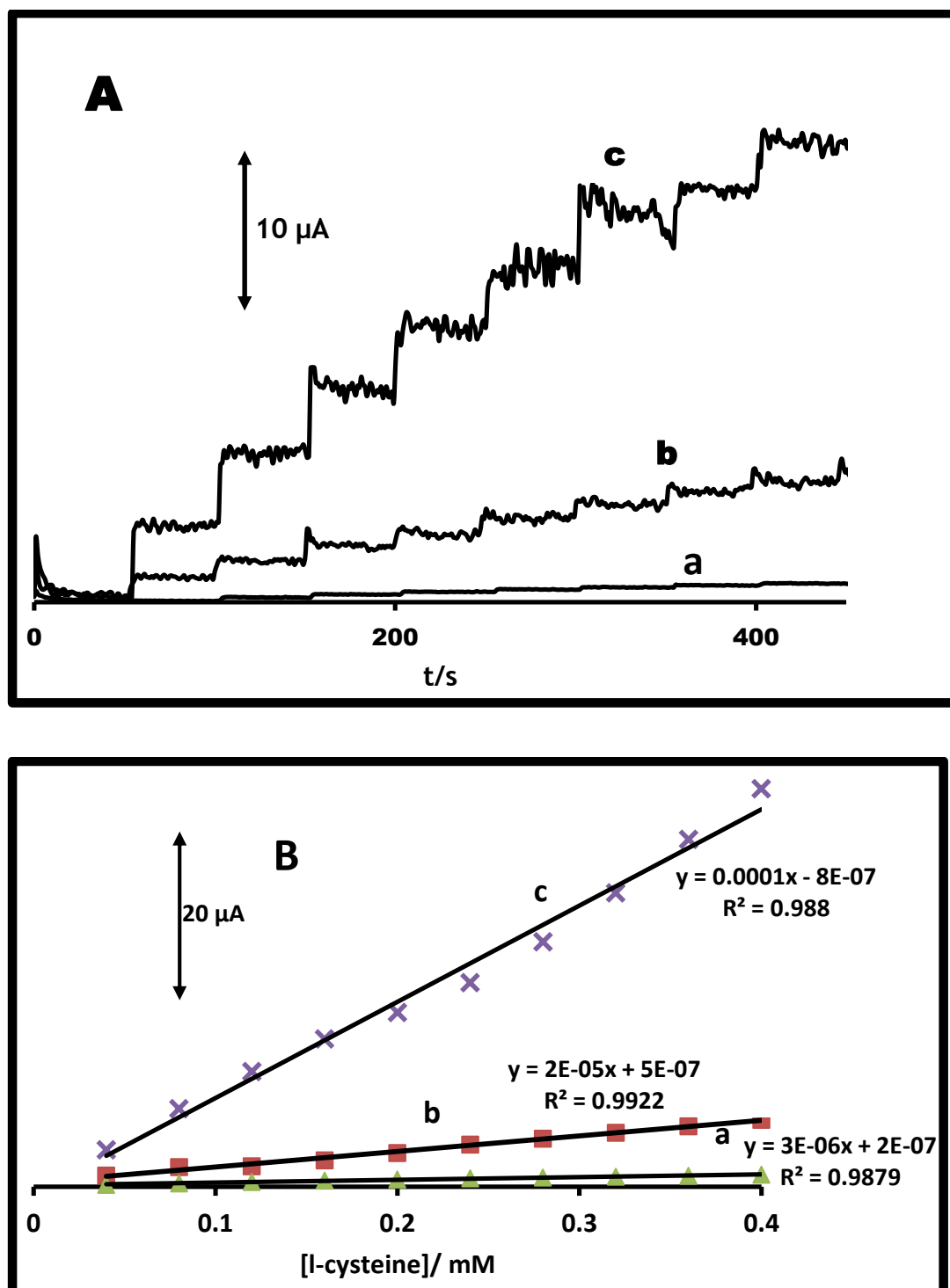


Fig. 5.3. Chronoamperometric steps (A) and plots of cumulative i_p vs [l-cysteine] (B) after addition of aliquots of 0.04 mM l-cysteine using bare GCE (a), CoTAPc-MWCNTs -GCE (mixed) (b), CoTAPc-MWCNTs -GCE (sequential) (c). pH 4 buffer.

Fig. 5.3A shows chronoamperograms for the pH 4 buffer using aliquots of 0.04 mM l-cysteine. There is tendency for more noise as the concentration of l-cysteine increases. The slopes of the plots in Fig. 5.3B give the sensitivity of the modified surfaces. LOD values were calculated using the 3σ -notation. The CoTAPc-MWCNTs (sequential) modified surface showed better sensitivity and LOD (Table 5.1) than CoTAPc and CoTAPc-MWCNTs (mixed) modified surfaces. The SECM studies discussed in chapter 4 explain the differences in the catalytic performance between the two surface modifications in terms of the active surface area available for catalysis. The rough CoTAPc-MWCNT (sequential) modified surface has more redox-active sites available to assist in electron transfer.

Therefore, the enhancement of the SECM tip current for CoTAPc-MWCNT (sequential) modified surface demonstrates high surface-to-volume ratio. The increase in electroactive surface area allows for lower detection limits and higher sensitivity to analytes [186], and this is in agreement with better detection limits and sensitivity values obtained by the CoTAPc-MWCNT (sequential) modified surface from CV and CA studies. By combining lower detection limits and shorter response times towards oxidation of l-cysteine {relative to CoTAPc, MWCNT and CoTAPc-MWCNT (mixed)}, CoTAPc-MWCNT (sequential) modified surfaces can be effectively used for the development of fast detection systems for l-cysteine at very low concentration levels. The calculated sensitivity and LOD values in Tables 5.1 were obtained by using 0.04 mM aliquots and within the concentration range of 0.04 mM to 0.4 mM of l-cysteine. The surfaces were further probed using smaller aliquots, 0.005 mM and concentration range 0.005 mM to 0.04 mM of l-cysteine, Fig. 5.4A(a).

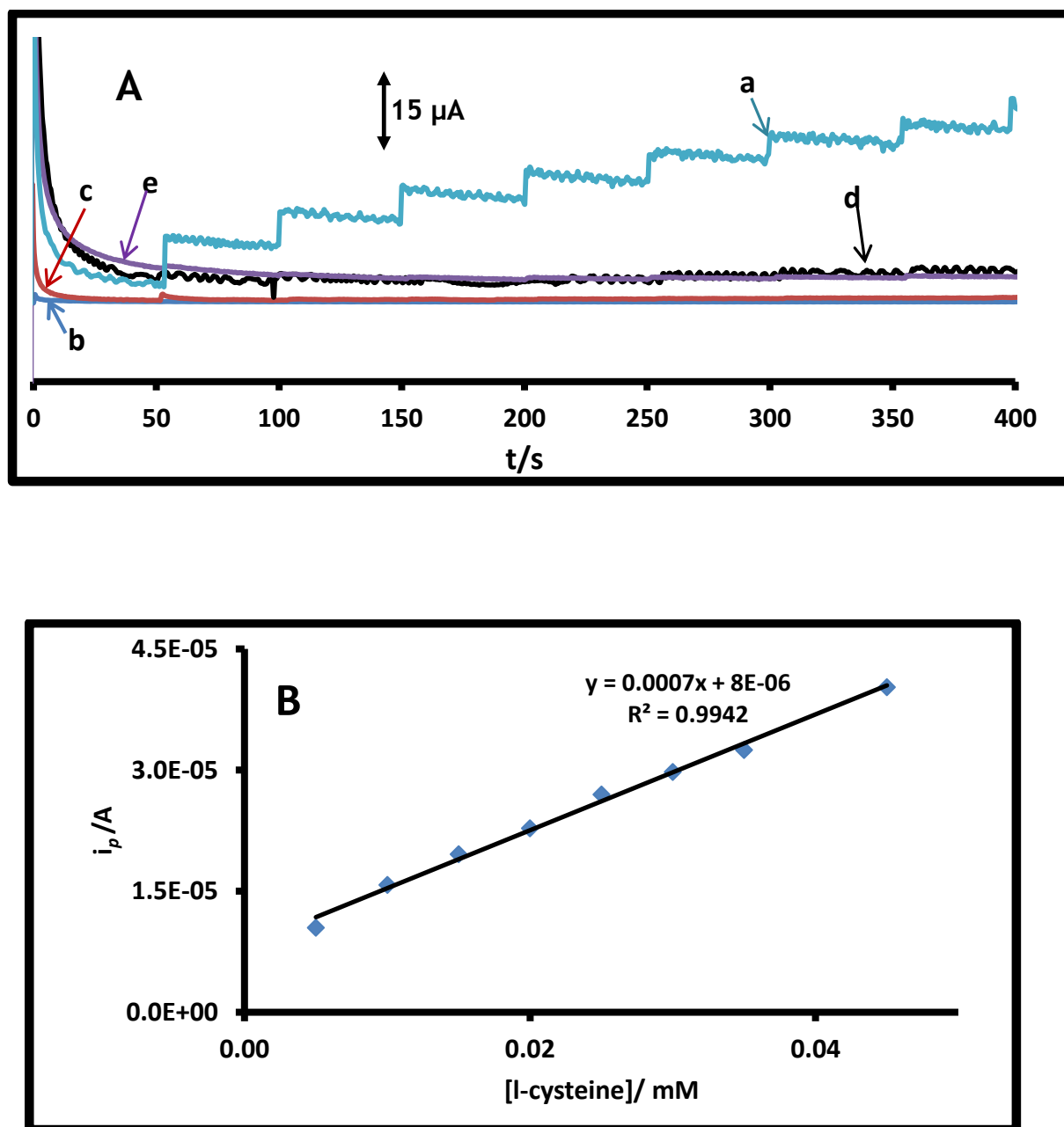


Fig. 5.4. (A) Chronoamperogram steps after addition of aliquots of 0.005 mM L-cysteine using bare BGE (a), CoTAPc (b), MWCNTs (c), CoTAPc-MWCNTs -GCE (mixed) (d), CoTAPc-MWCNTs -GCE (sequential) (e). pH 4 buffer. (B) Plots of i_p vs. [l-cysteine] after addition of aliquots of 0.005 mM l-cysteine using CoTAPc-MWCNTs-GCE (sequential) in pH 4 buffer.

The step sizes in Fig. 5.4A (a) are uniform for sequential, confirming the stability of the electrode as also shown by Fig. 5.2C. At this low concentration, only the CoTAPc-

MWCNT (sequential) surface gave distinct chronoamperogram steps, Fig. 5.4A (a), and the calculated LOD was 2.8×10^{-7} M, Table 5.1. Fig. 5.4B was plotted from CoTAPc-MWCNT (sequential) chronoamperometry steps to obtain a better sensitivity value of 7.0×10^{-4} A/mM of l-cysteine, Table 5.1. This makes the CoTAPc-MWCNT (sequential) surface a better candidate for fabricating surfaces for sensing. To confirm the ability of the modified surface to detect l-cysteine at the predetermined LOD of 2.8×10^{-7} M, Table 5.1, CA studies were performed at this concentration. There was no distinct chronoamperometry step at this LOD, however at a concentration of 4.0×10^{-7} M l-cysteine a distinct step was obtained (Fig. 5.5).

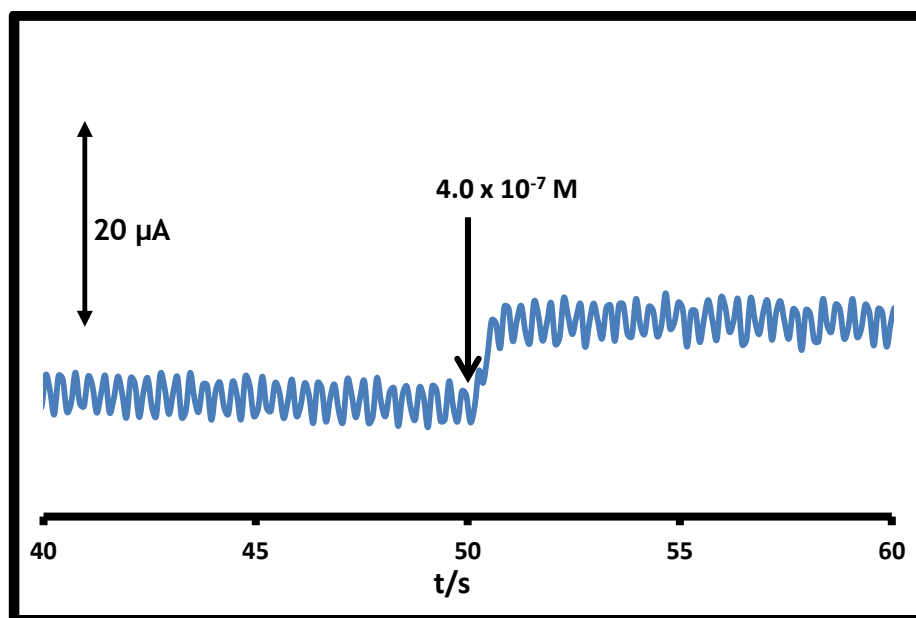


Fig. 5.5. Chronoamperomogram step after addition of an aliquot of 0.0004 mM l-cysteine using CoTAPc-MWCNTs -GCE (sequential) in pH 4 buffer.

The chronoamperometry results also show good stability as the modified surface can be used for several times (as judged by distinct steps) before it loses its catalytic

efficiency with or without reconditioning, Fig. 5.6b-d. Reconditioning was done through rinsing the electrode surface with Milli-Q water before the next cycle of chronoamperometry steps is repeated.

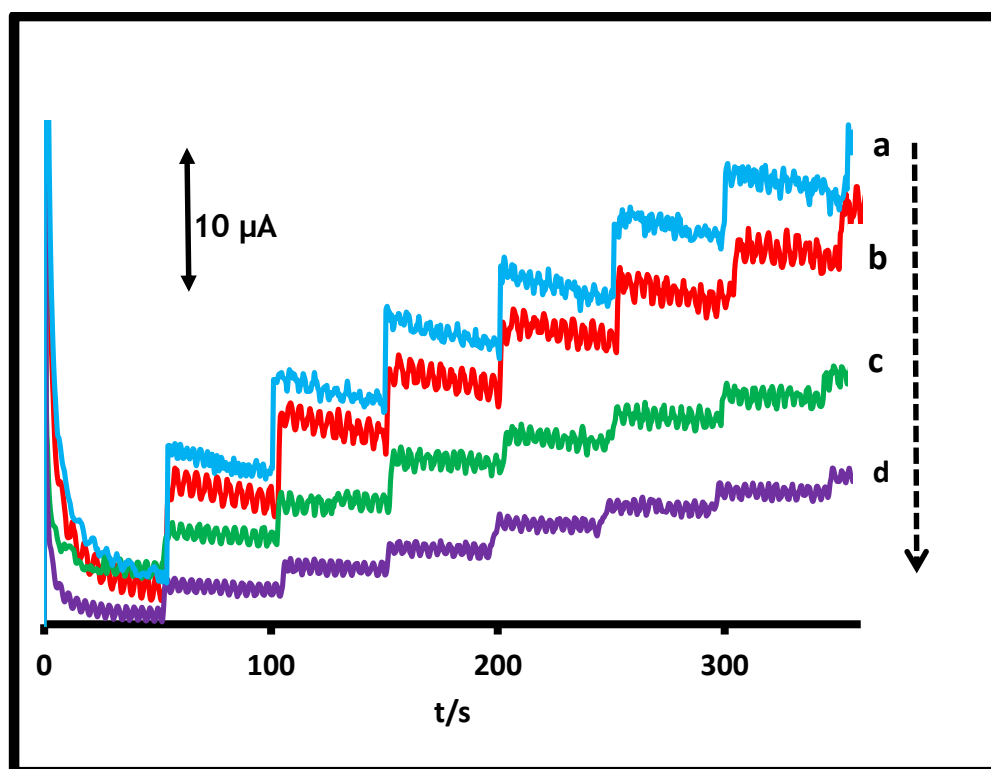


Fig. 5.6. Chronoamperomogram steps for CoTAPc-MWCNTs -GCE (sequential) after successive addition of 0.005 mM L-cysteine (a), steps after 1st reconditioning (b), steps after second reconditioning (c) steps after third reconditioning (d). pH 4 buffer.

In comparison to the first chronoamperometry steps for CoTAPc-MWCNT (sequential) using 0.005 mM L-cysteine, Fig. 5.6a, there was an observable 16% (Fig. 5.6b) decrease in peak currents after the first reconditioning, 47% (Fig. 5.6c) after the second reconditioning and 70% (Fig. 5.6d) after the third reconditioning. It is worth-

noting that even after the third reconditioning; the chronoamperometry steps were still distinct unlike other surfaces described in this work.

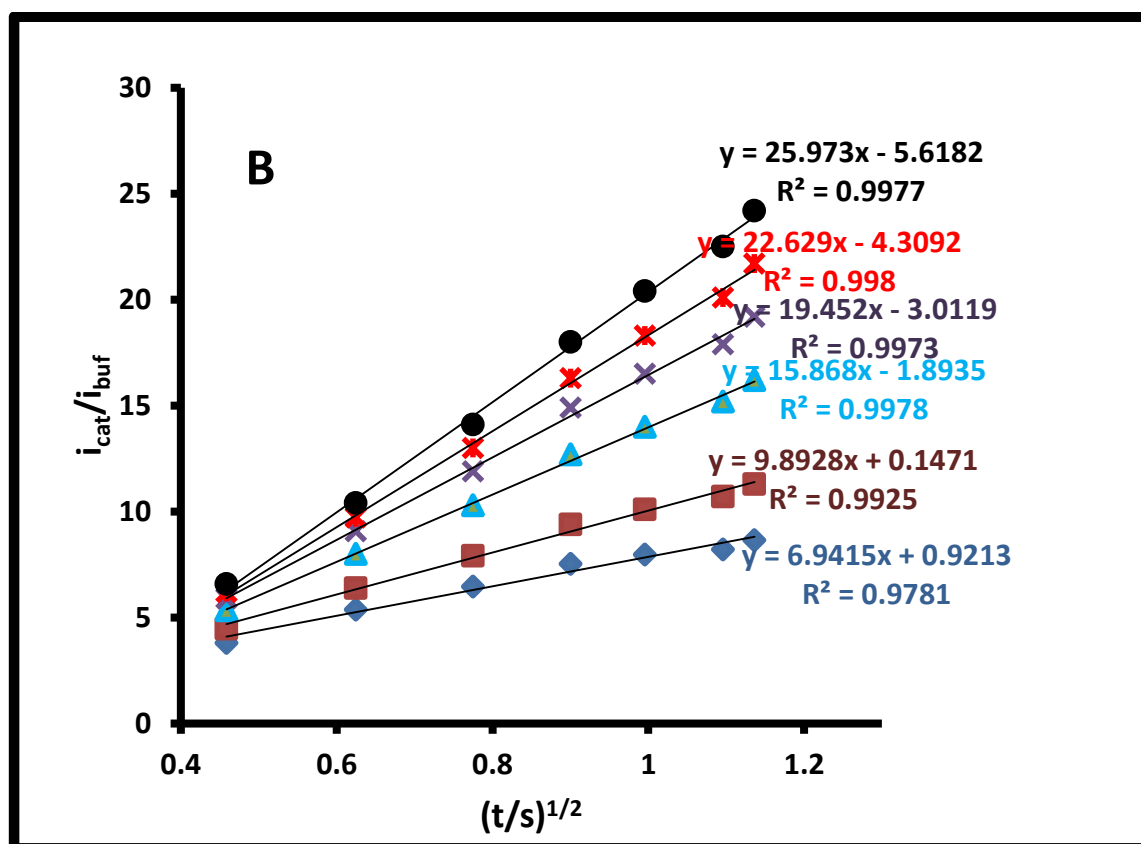
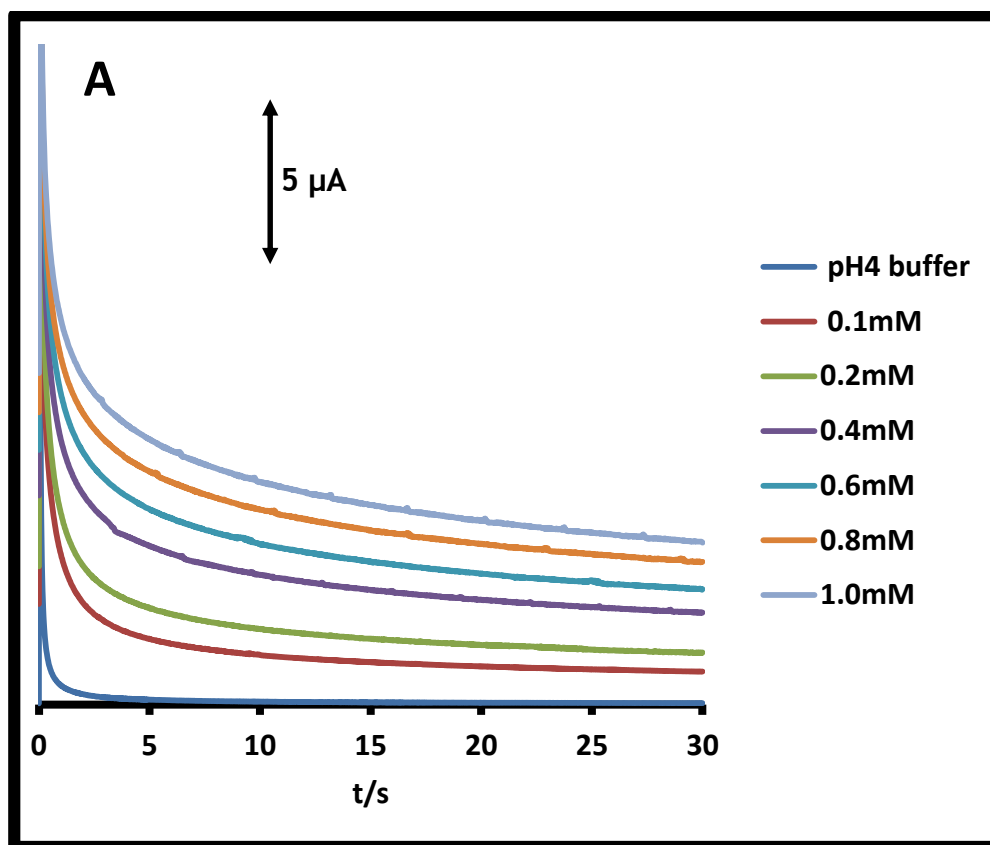
The rate constant (k) for the detection of l-cysteine on surface confined CoTAPc-MWCNTs (sequential) was determined according to the method described in the literature [187], equation 5.2.

$$\frac{i_{\text{cat}}}{i_{\text{buf}}} = \gamma^{1/2} \left[\pi^{1/2} \text{erf}(\gamma^{1/2}) + \frac{\exp(-\gamma)}{\gamma^{1/2}} \right] \quad (5.2)$$

where $\gamma = kC_0t$ (C_0 is the bulk concentration of l-cysteine) and $\text{erf}(\gamma^{1/2})$ is the error function. In cases where γ exceeds 2, [187] the error function is almost equal to 1 and equation 5.2 reduces to equation 5.3:

$$\frac{i_{\text{cat}}}{i_{\text{buf}}} = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kC_0t)^{1/2} \quad (5.3)$$

where i_{cat} and i_{buf} are currents in the presence and in the absence of l-cysteine, k = catalytic rate constant ($\text{M}^{-1}\text{s}^{-1}$) for the oxidation of l-cysteine, and t = elapsed time/s. Fig. 5.7B shows the linear relationships for the $i_{\text{cat}}/i_{\text{buf}}$ vs. $t^{1/2}$ plots for the different l-cysteine concentrations, obtained from the chronoamperomogram in Fig. 5.7A. The calculations were done using data obtained from $t/\text{s} = 0.46$ to 1.23. The slopes of these plots were plotted against the concentration of l-cysteine to give another linear relationship shown in Fig. 5.7C. The slope of Fig. 5.7C is equal to πk , and this gives a k -value of $2.2 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.



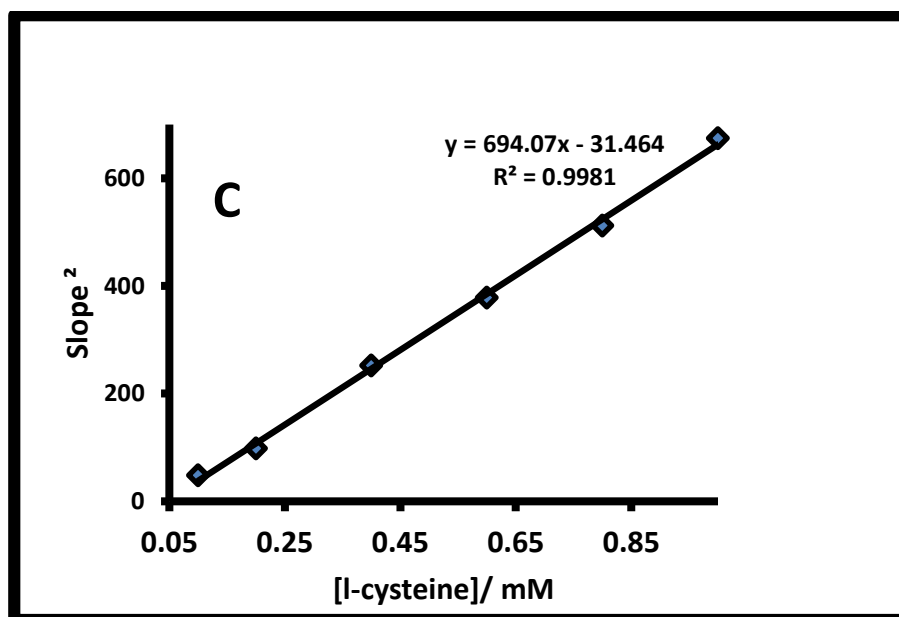


Fig.5.7. (A); Chronoamperomograms for different l-cysteine concentration, (B); Plot of i_{cat}/i_{buf} vs. $t^{1/2}$, (C) Plot of slope² vs. [l-cysteine]. (Data collected using CoTAPc-MWCNTs (sequential)).

The value of k is larger than that obtained for l-cysteine on indigo carmine modified GCE ($5.9 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) [188] and on Nile blue A modified ($1.93 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$) [189]. This indicates a faster rate of oxidation at the surface of the modified electrode, thereby making it a suitable candidate for the fabrication of a sensor for the fast detection of l-cysteine.

5.1.1.3. EIS.

EIS was used to determine the charge transfer resistance (R_{ct}) and gives information on the electron transfer kinetics in the presence of l-cysteine. The Nyquist representations are shown in Fig. 5.8A and Bode plots in Fig. 5.8B. Fig. 5.8C represent the equivalent circuit for fitting and obtaining EIS data.

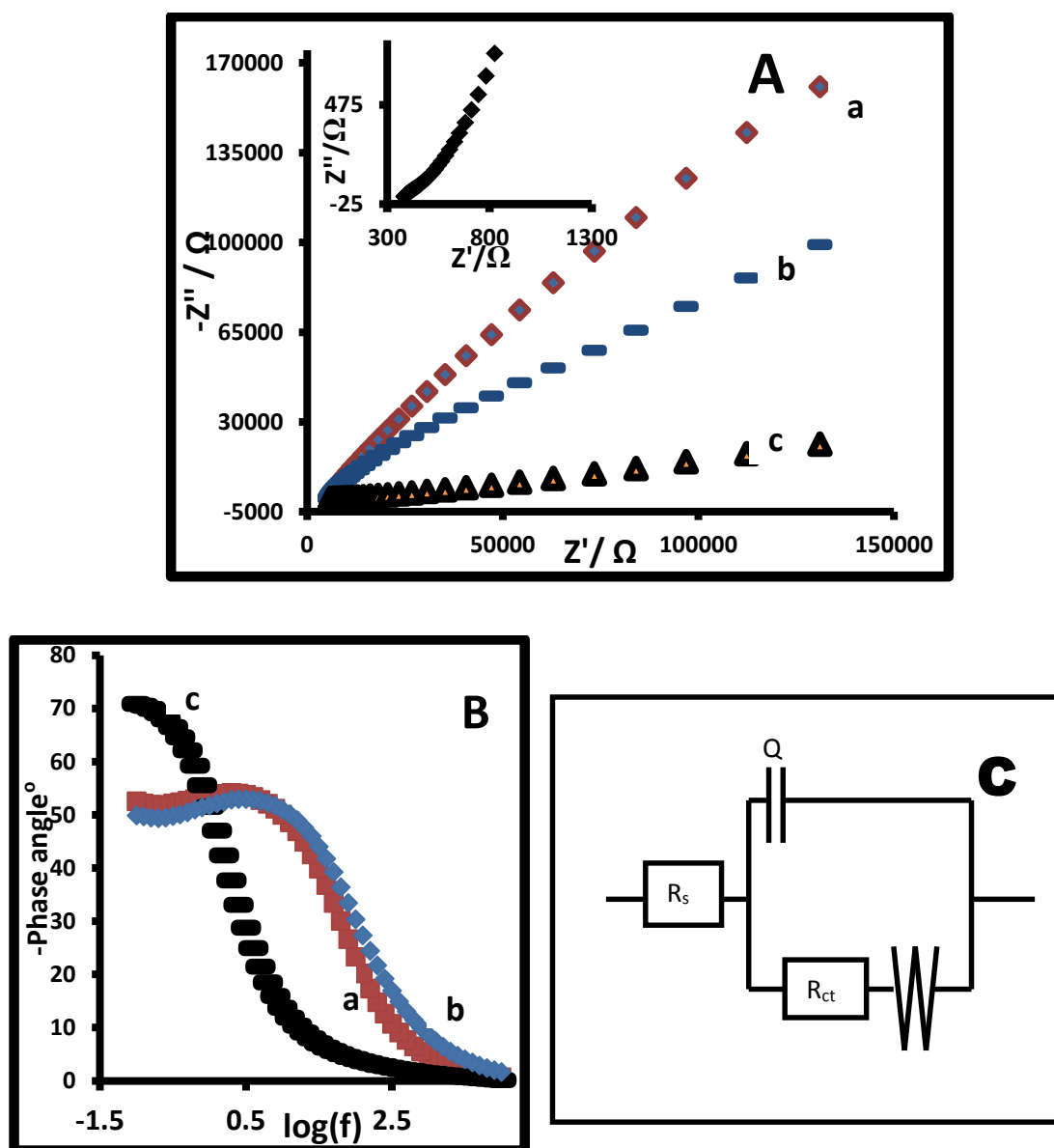


Fig. 5.8. Nyquist plots (A) for bare GCE (a), CoTAPc-MWCNTs (mixed) (b), CoTAPc-MWCNTs (sequential) (c), inset = expansion of the high frequency region for (c). Bode presentations (B) for bare GCE (a), CoTAPc-MWCNTs (mixed) (b), CoTAPc-MWCNTs (sequential) (c), and Equivalent circuit in which Warburg impedance is important (C). Analyte = 0.05 mM L-Cysteine, pH 4 buffer.

Table 5.2 gives comparative R_{ct} values obtained from the Nyquist plot. The EIS parameters were obtained by fitting the Randles equivalent circuit (Fig. 5.8C) to the experimental data and performing complex nonlinear least-squares procedures available in EIS data fitting computer programme.

Table 5.2. A summary of R_{ct} ($k\Omega$), n , and k_{app} (cms^{-1}) values for the different surfaces in 0.05 mM l-cysteine in pH 4 buffer.

Electrode	R_{ct} ($k\Omega$)	n	k_{app} (cms^{-1})
Bare GCE	2.15 (± 16 %)	0.87(± 3 %)	5.3×10^{-2}
CoTAPc	2.04 (± 15 %)	0.89(± 3 %)	5.5×10^{-2}
CoTAPc-MWCNTs (premixed)	1.98 (± 22 %)	0.89(± 4 %)	5.7×10^{-2}
CoTAPc-MWCNTs (sequential)	1.56 (± 22 %)	0.84(± 1 %)	7.3×10^{-2}

EIS data shows that there was a small decrease in R_{ct} for CoTAPc compared to bare GCE, showing a slightly improved electron transfer for the former. There was a significant decrease in the R_{ct} for CoTAPc-MWCNTs (mixed) and CoTAPc-MWCNTs (sequential) relative to the bare GCE, Table 5.2. R_{ct} is much smaller for CoTAPc-MWCNTs (sequential) showing good conductivity of such a modified surface. When looking at the impedance Nyquist plot (Fig. 5.8A), it is observed that the semicircular regions are not well defined, but for bare GCE and CoTAPc-MWCNTs (mixed) the circles are clearer than for CoTAPc-MWCNTs (sequential). However, the R_{ct} values were estimated by expanding the high frequency region for CoTAPc-MWCNT (sequential), with errors shown in Table 5.2 (see insert in Fig. 5.8A for the

expansion). If the chemical system is kinetically rather sluggish, it will show a large R_{ct} , and may display only a very limited-frequency region where mass transfer is a significant factor [169].

The results show the other extreme in which R_{ct} is inconsequently small by comparison to the ohmic resistance and the Warburg impedance resulting in semicircular plots which are not well defined. This is also a confirmation that the catalytic reaction at the electrode surfaces is mass transfer or diffusion controlled as predicted earlier by results of the plot of i_p vs. $v^{1/2}$ (Fig. 5.2A) which was linear i.e. the system is kinetically facile and mass transfer plays a major role. A plot of phase-shift vs. log frequency (Fig. 5.8B) provides extra information on frequency which cannot be obtained from the Nyquist plot. The phase angle values for all the bare GCE, premixed and sequential electrode surfaces studied in this work are less than the ideal 90° for a true capacitor [178]. Surfaces with the phase angle shifted towards lower frequencies in the Bode plot indicate better catalytic efficiency; hence the Bode plot further confirms better catalytic activity of CoTAPc-MWCNTs (sequential) modified surface towards the oxidation of l-cysteine. The phase angle for CoTAPc-MWCNTs (mixed) and the bare GCE for Fig. 5.8B(a) and Fig. 5.8B(b) are almost at the same frequency. The CoTAPc-MWCNTs (mixed) surface gave a phase angle of 50° which is lower than the phase angle for the bare GCE (55°). CoTAPc-MWCNTs (sequential) has a phase angle of 72° . Such changes in phase angles and frequencies are a clear-cut indication of the structural differences of the surfaces, and that oxidation of the analyte occurred at the modified surfaces rather than on the bare GCE. This also serves to explain the differences in the catalytic activity

observed from the other techniques explained in sections above. Furthermore the n -values are in the range 0.84-0.89 (Table 5.2). When $n = 1$, this means that the surface behaves more like a capacitor. Therefore, these results show that all the tailored surfaces used have non-capacitive features. It is also important to note that none of the surfaces gave a value of $n = 0$ which is typical of a resistor, hence the surfaces were behaving like conductors. The apparent electron transfer rate constants (k_{app}) were also calculated, using equation 4.5 [179], for the different electrode surfaces towards oxidation of l-cysteine (where [l-cysteine] = 0.05 mM) to confirm CV and CA data. K_{app} values are shown in Table 5.2

The surface area was obtained using ferricyanide redox probe through the Randles-Sevcik equation 4.2 [169]. Again, CoTAPc-MWCNTs (sequential) and CoPyPc-MWCNT (linked) showed the fastest electron transfer processes, Table 5.2.

5.1.2. Poly CoTAPc and poly CoPyPc.

5.1.2.1. RDE.

The kinetics of electrooxidation of l-cysteine was performed by hydrodynamic RDE voltammetry technique (in addition to CV discussed above) as representative, in 8 mM l-cysteine. Fig. 5.9A shows comparative RDE voltamograms for the behaviour of bare GCE, poly-CoPyPc and poly-CoPyPc-MWCNT. There was no electrooxidation of l-cysteine on a bare GCE within this potential window in pH 4 buffer.

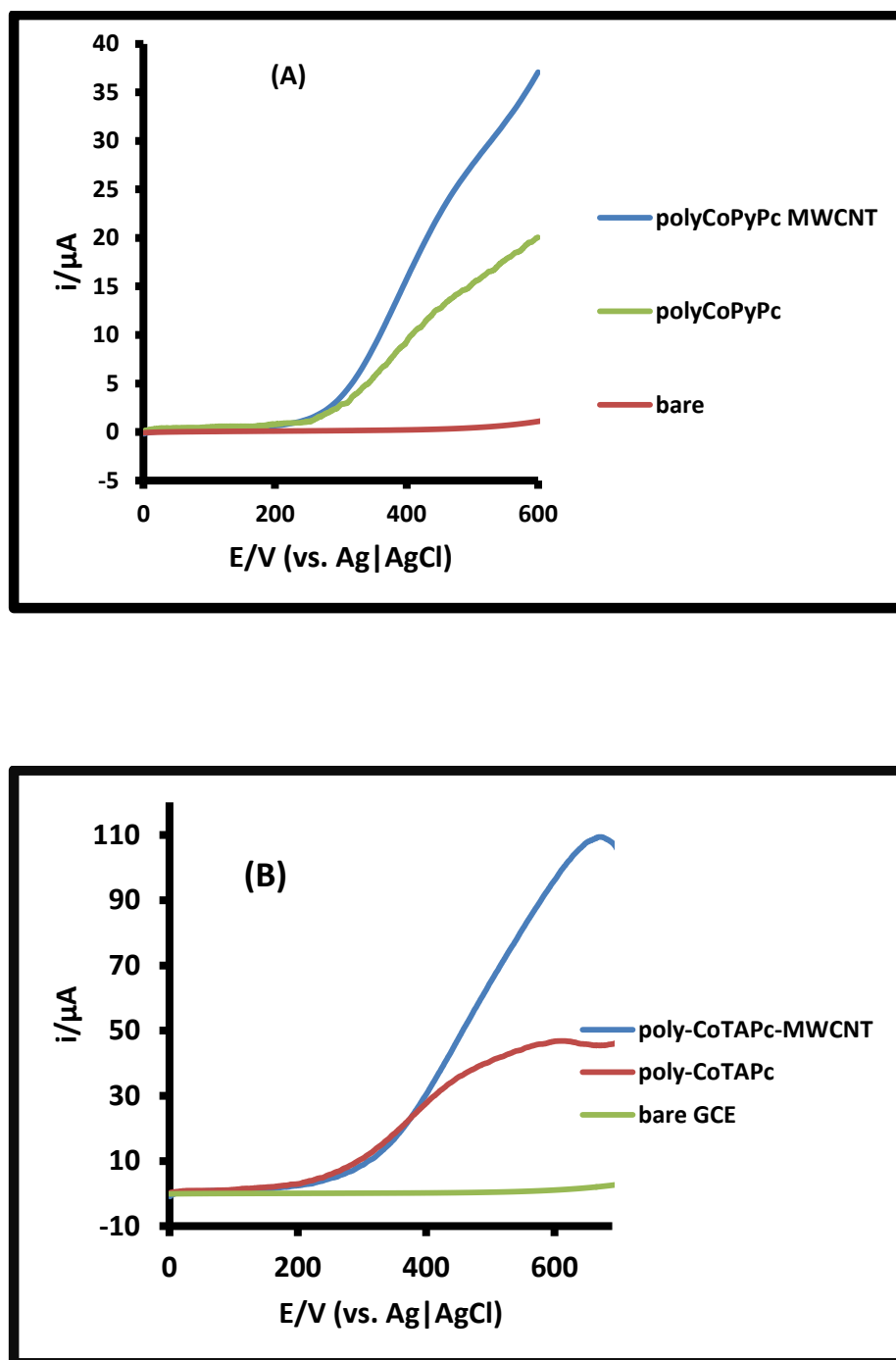


Fig. 5.9. Comparative RDE voltammograms for 8 mM L-cysteine at (A) bare GCE, poly-CoPyPc and poly-CoPyPc-MWCNT surfaces and (B) bare GCE, poly-CoTAPc, and poly-CoTAPc-MWCNT surfaces. Scan rate = 10 mV/s, rotational speed = 400 rpm.

There was a distinct and remarkable activity observed from poly-CoPyPc relative to the bare GCE. It was also interesting to note that the poly-CoPyPc-MWCNT nanocomposite gave much higher limiting currents than poly-CoPyPc for the electrooxidation of l-cysteine, indicating the importance of polymerizing the MPc over a MWCNT platform than on a bare GCE. The same behaviour in which limiting currents doubled in the presence of MWCNT was also observed with poly-CoTAPc and poly-CoTAPc-MWCNT, Fig. 5.9B.

RDE voltammograms for the electrooxidation of l-cysteine were also recorded at varying rotational speeds for all the four electrocatalysts, Fig. 5.10 (using poly-CoTAPc as an example). The inset in Fig. 5.10A shows the Levich plots (i_L vs. $\omega^{1/2}$) obtained from the Levich equation (eqn 4.4). The plots show the expected linear dependence of the limiting currents against square root of rotational speed predicted by the Levich equation, indicative of diffusion controlled mass transport. Further kinetic details of the electrooxidation of l-cysteine on these catalysts were derived from the Koutecky-Levich equation (eqn 4.3). The intercepts of the Koutecky-Levich plots (i^{-1} vs. $\omega^{-\frac{1}{2}}$) shown in Fig. 5.10B were used for determination of the kinetic reaction rate constants (summarised in Table 5.3) for the electrooxidation of l-cysteine at the polymer film surfaces.

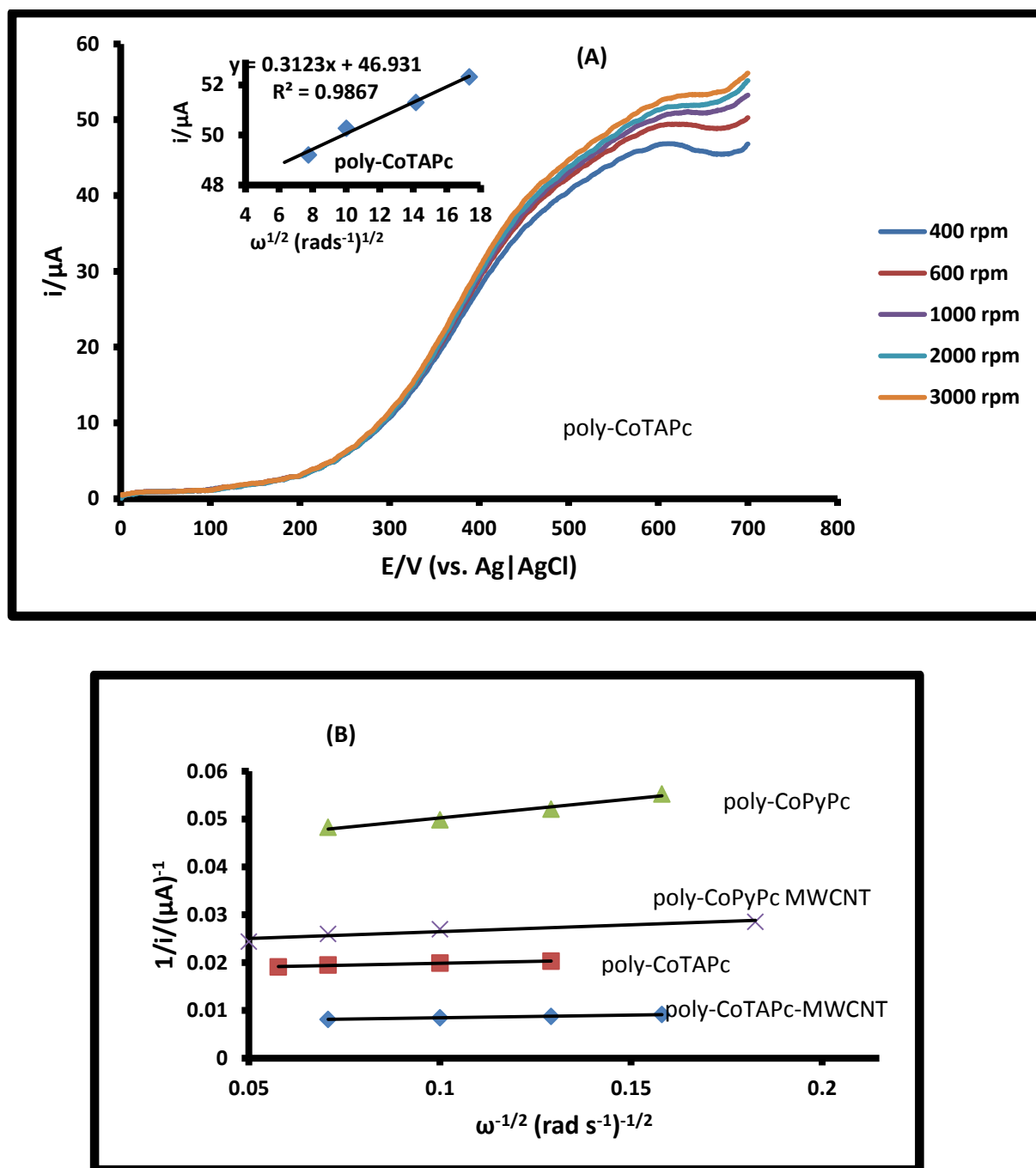
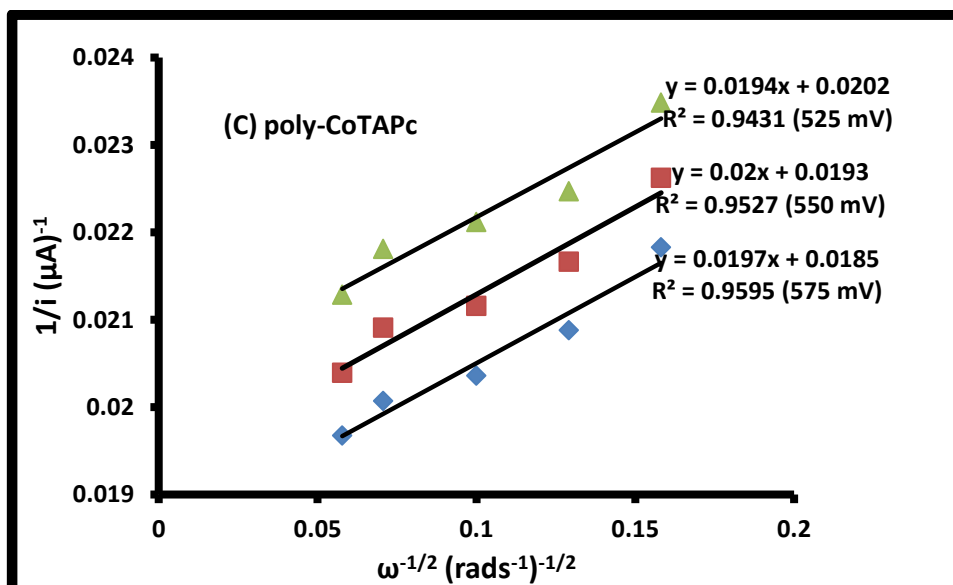
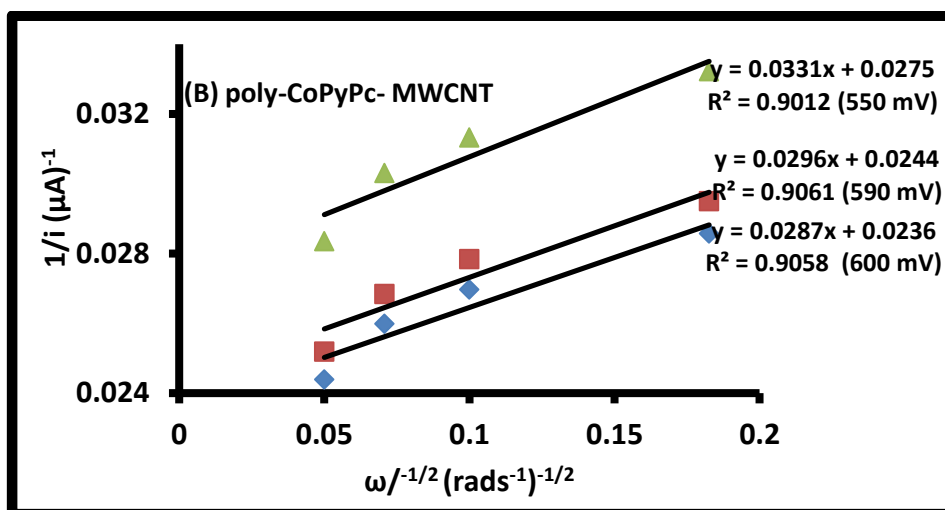
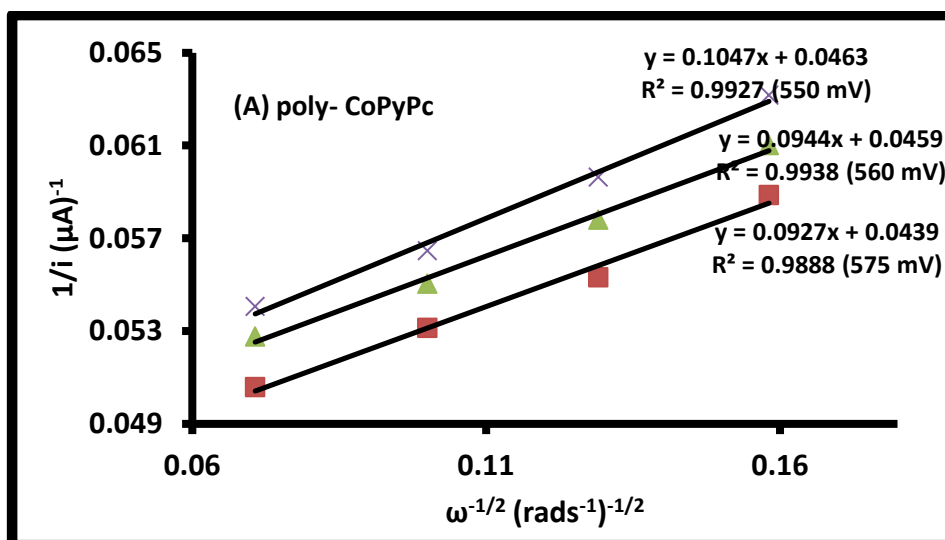


Fig.5.10. (A) RDE voltammograms of 8 mM l-cysteine on poly-CoTAPc at different rotation rates. Scan rate = 10 mV/s, Inset = Levich plot for the film. (B) Koutecky-Levich plots for the electrooxidation of 8 mM l-cysteine in pH 4 buffer on polymer films.

Table 5.3. A summary of kinetic reaction rate constant (k) values for the different surfaces in 8 mM l-cysteine in pH 4 buffer.

Electrode	k (cms ⁻¹)
CoPyPc-MWCNT (linked)	1.50×10^{-4}
poly-CoTAPc-GCE	6.16×10^{-4}
poly-CoTAPc-MWCNT-GCE	1.54×10^{-3}
poly-CoPyPc-GCE	2.66×10^{-4}
poly-CoPyPc-MWCNT-GCE	4.33×10^{-4}

The rate constants values show that the rate of electrooxidation of l-cysteine was greatly improved when the polymers were formed on MWCNT, making nanocomposite electrocatalysis more favourable than individual polymers. The higher k values for poly-CoTAPc and poly-CoTAPc-MWCNT are consistent with surface coverage data. This suggests that their porosity is higher than poly-CoPyPc and poly-CoPyPc-MWCNT, leading to the observed better current responses. Reaction kinetics in terms of the order of reaction with respect to the test analyte were obtained from the plot of i^{-1} vs. $\omega^{-1/2}$ (Fig. 5.11A-D), where i is the current taken from the rising part the RDE voltammograms in Fig. 5.10A at the specified potentials shown in brackets. Parallel lines with almost constant slopes were obtained, illustrating a first order reaction with respect to l-cysteine electrooxidation.



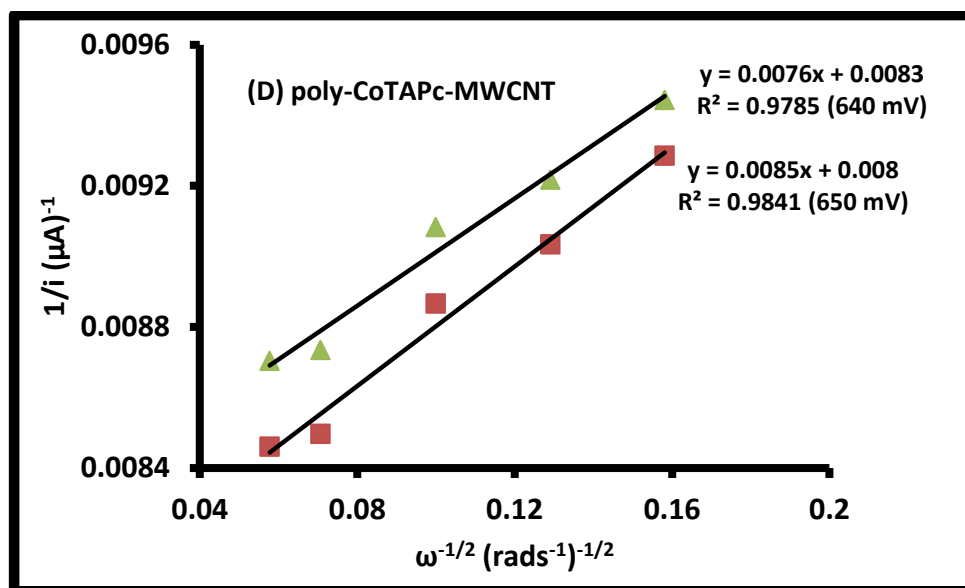


Fig. 5.11. Plots of $1/i$ vs. $\omega^{-1/2}$ from RDE voltammograms of 8 mM l-cysteine on (A) poly-CoPyPc, (B) poly-CoPyPc-MWCNT, (C) poly-CoTAPc and (D) poly-CoTAPc-MWCNT at different rotational speeds at the specified potentials values.

5.1.2.2. Cyclic voltammetry.

Fig. 5.12 (using poly-CoPyPc as an example) shows the cyclic voltammograms of l-cysteine in pH 4 buffer solutions on bare GCE and poly-CoPyPc-MWCNT. The individual polymers of CoPyPc and CoTAPc were not investigated further since they proved to be less electroactive than their respective polymeric nanocomposites. No peak was obtained with the bare GCE within this potential window in pH 4 buffer. Irreversible oxidation peaks were observed on thin polymer film nanocomposites. The electrooxidation peaks on poly-CoTAPc-MWCNT and poly-CoPyPc-MWCNT were observed at approximately 0.40 V and 0.55 V, respectively. These values are much lower than observed for the oxidation of l-cysteine (in acid media) on monomeric (adsorbed) CoPc derivatives alone (~ 0.8 V) [120]. Thus, nanocomposites involving

polymeric MPcs have better electrocatalytic properties than monomeric MPcs thin films. The electrocatalytic oxidation peaks in both cases were observed in the potential region close to the $\text{Co}^{\text{III/II}}$ redox couple, implying that electrocatalysis is mediated by this redox couple. The mechanism will be as proposed before [120] in acid media.

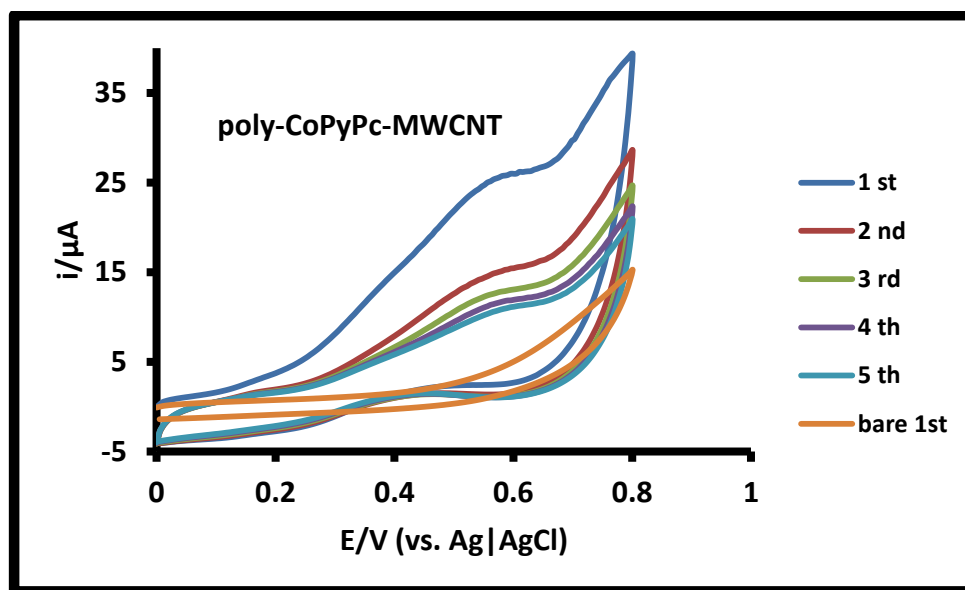


Fig. 5.12. Comparative cyclic voltammograms of 8 mM l-cysteine in pH 4 buffer at a bare GCE and poly-CoPyPc-MWCNT-GCE. Scan rate = 100 mV/s.

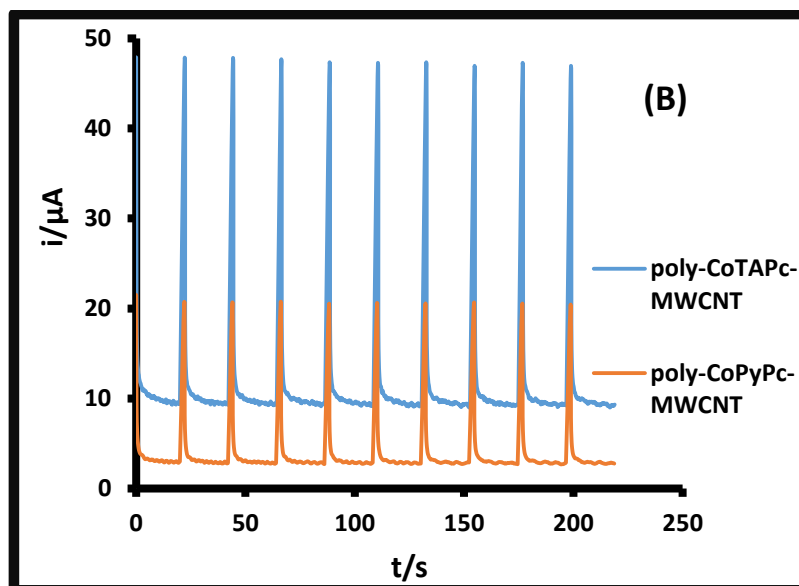
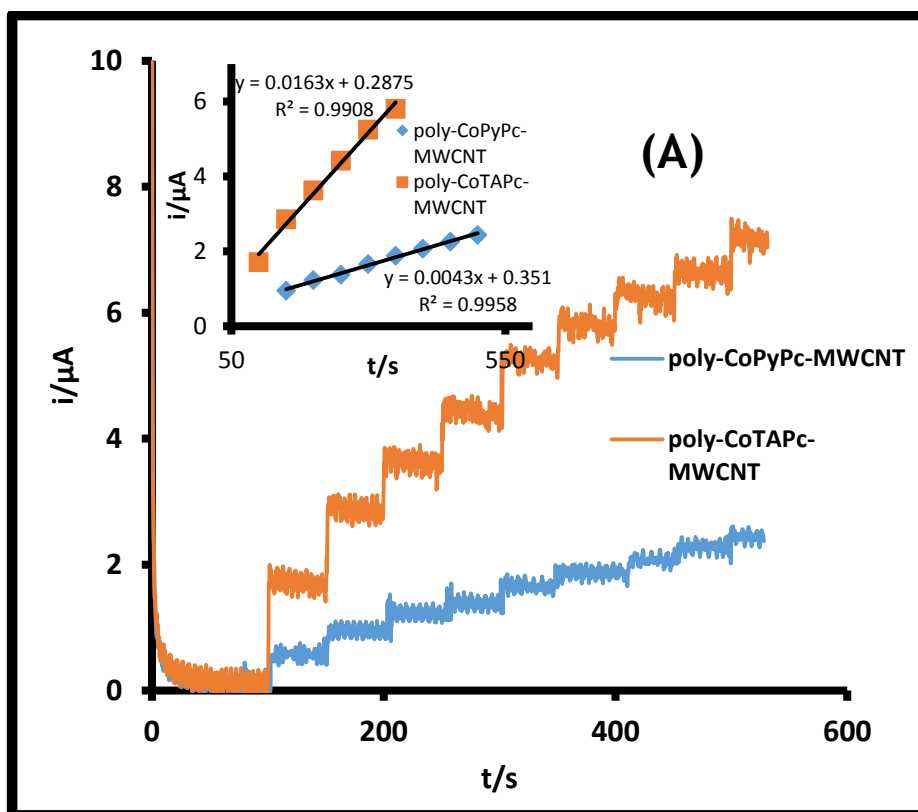
5.1.2.3. Chronoamperometry studies.

Chronoamperometry technique was used to gain more information on analytical parameters such as limit of detection (LOD), sensitivity and further confirmation of electrode surface stability for these thin polymer films.

The chronoamperometry steps produced upon addition of 0.03 mM l-cysteine aliquots are shown in Fig. 5.13A. Poly-CoTAPc-MWCNT nanocomposite film showed better catalytic current responses than poly-CoPyPc-MWCNT nanocomposite film.

The differences in the rate of increase of catalytic current with time are clearly shown by slopes of the plots of cumulative step currents against time, Fig. 5.13A inset. Furthermore, the catalytic step currents remain higher and stable for poly-CoTAPc-MWCNT nanocomposite film. Stability tests were done by performing ten chronoamperometry scans in 0.27 mM l-cysteine (Fig. 5.13B). Both surfaces showed very stable catalytic currents for the ten chronoamperometry scans, however poly-CoTAPc-MWCNT nanocomposite film gave higher catalytic currents as observed in Fig. 5.13A.

From the plots of current vs. concentration of l-cysteine (Fig. 5.13C), sensitivity and LOD parameters were derived. Under these hydrodynamic conditions, poly-CoTAPc-MWCNT film was more sensitive ($27.11 \mu\text{A}/\text{mM}$ l-cysteine) than poly-CoPyPc-MWCNT film ($7.09 \mu\text{A}/\text{mM}$ l-cysteine). The LOD of detection for poly-CoTAPc-MWCNT and poly-CoPyPc-MWCNT were found (using the 3σ notation) to be $1.74 \times 10^{-8} \text{ M}$ and $3.55 \times 10^{-8} \text{ M}$, respectively, Table 5.1. These values are well below the LOD observed on monomeric CoTAPc supported on MWCNT (at $7.3 \times 10^{-7} \text{ M}$), Table 5.1, implying polymeric MPcs are better candidates for fabrication of MPc-MWCNT nanocomposite electrocatalysts. It is also interesting to note that the levels of l-cysteine in human beings $\sim 250 \mu\text{M}$ [190], are far much higher than the LODs reported here. This makes clinical applications at levels lower than $250 \mu\text{M}$ so much accessible at these thin polymer nanocomposite films.



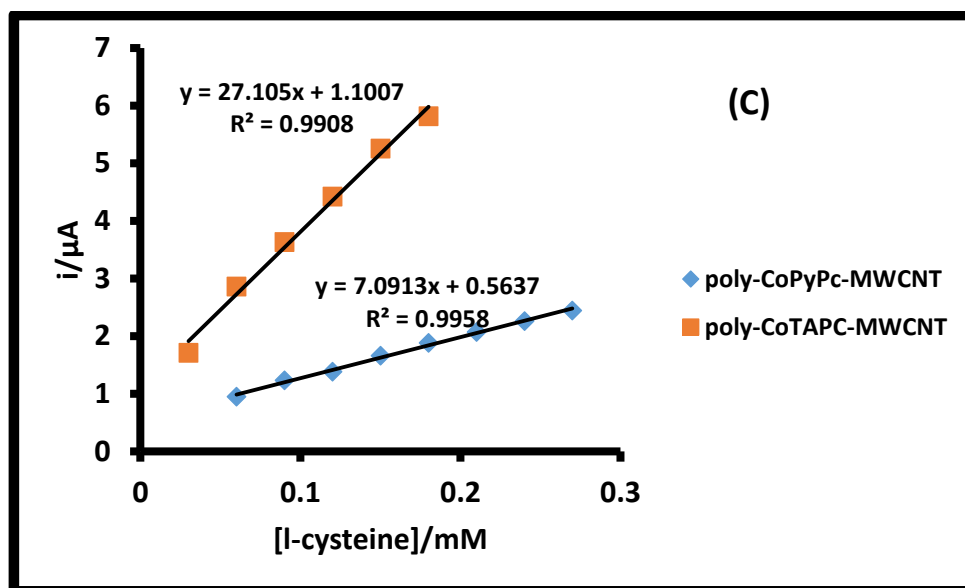


Fig. 5.13. (A) Electrooxidation chronoamperomogram steps at poly-CoPyPc-MWCNT and poly-CoTAPc-MWCNT thin films after successive additions of aliquots of l-cysteine in pH 4 buffer. (B) Repetitive chronoamperomograms in 0.27 mM l-cysteine in pH 4 buffer using poly-CoPyPc-MWCNT (red) and poly-CoTAPc-MWCNT (blue) thin films. (C) Plots of cumulative electrooxidative currents after addition of aliquots of 0.03 mM l-cysteine using poly-CoPyPc-MWCNT and poly-CoTAPc-MWCNT thin films.

5.1.3. CoPyPc-MWCNT nanocomposites.

5.1.3.1. RDE.

The hydrodynamic RDE technique was then used to gather information on electron transfer kinetics at different modified surface for the practical electrooxidation of l-cysteine. This was done to compare nanocomposites fabricated through chemical linking to those made by mixing. Fresh catalyst films were used for each RDE voltammogram at each rotational speed. Fig. 5.14 (inset) shows the RDE

voltammogram for MWCNT-COOH. There was no well-defined electrooxidation of L-cysteine within this potential window. The kinetics of the mixed nanocomposite were not evaluated further for RDE since its performance in $\text{Fe}(\text{CN})_6^{3-/4-}$ was relatively poor than the linked nanocomposite.

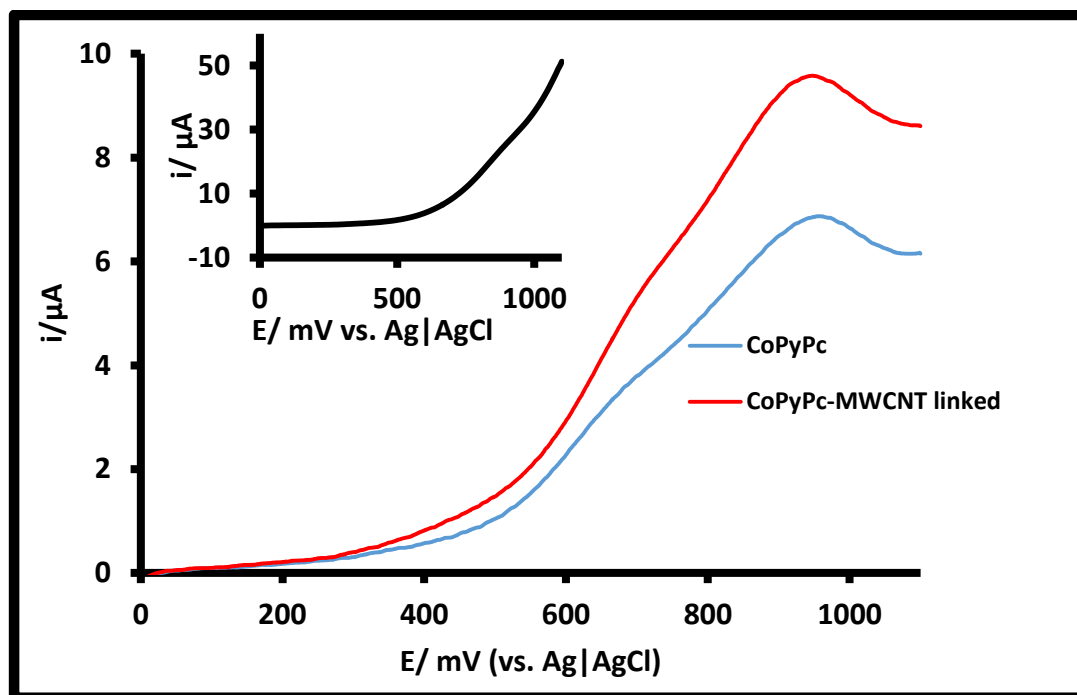


Fig. 5.14. Comparative RDE voltammograms for the electrooxidation of 8 mM L-cysteine on MWCNT-COOH (inset), CoPyPc (blue), and linked CoPyPc-MWCNT (red) modified surfaces. Scan rate = 10 mV/s; ω = 1000 rpm. pH 4.

CoPyPc demonstrated electrooxidation activity on L-cysteine as shown in Fig. 5.14. This demonstrates that electrocatalysis occurs mainly at the CoPyPc surface than MWCNT. However, the linked nanocomposite of CoPyPc and MWCNT (CoPyPc-MWCNT linked) showed improved electrooxidation behavior than its individual components. The catalytic currents improved by approximately 35 % when CoPyPc was anchored on MWCNT than directly onto GCE. This suggests that MWCNT provide a good

catalytic platform for the performance of CoPyPc than a bare GCE. The calculated kinetic rate constant for the electrooxidation of L-cysteine by the linked CoPyPc-MWCNT nanocomposite was found to be $1.50 \times 10^{-4} \text{ s}^{-1}$ (Table 5.3) using equation 4.3 and a figure similar to Fig. 5.10. The value was lower than for poly-CoPcs, showing the superiority of polymerisation in nanocomposite making. The Levich plot for the electrooxidation of L-cysteine on covalently linked CoPyPc-MWCNT thin film surface is shown as an inset in Fig. 5.15, and the linear dependence of i_L vs. $\omega^{1/2}$ is consistent with a diffusion controlled activity at the catalyst film surface.

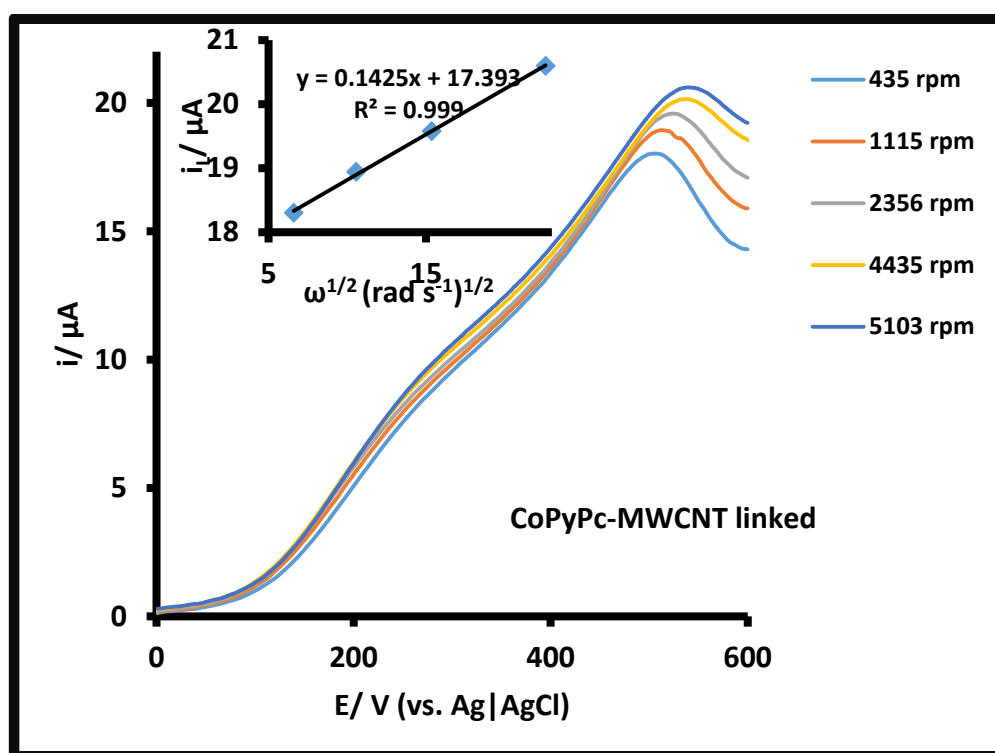


Fig. 5.15. Comparative RDE voltammograms for the electrooxidation of 8 mM L-cysteine on linked CoPyPc-MWCNT modified surface at different rotational speeds. Scan rate = 10 mV/s. Inset = Levich plot.

Plot of i^{-1} vs. $\omega^{-1/2}$ (figure not shown but similar to Fig. 5.11), where current was taken from the rising part of voltammograms in Fig. 5.15, resulted in nearly parallel straight lines, implying a first order reaction with respect to l-cysteine electrooxidation.

5.1.3.2. Cyclic and Square Wave voltammetry.

The nanocomposites (mixed and linked) showed two oxidation peaks in the regions labeled I and II (Fig. 5.16A) in the presence of l-cysteine. The bare GCE surface (Fig. 5.16A inset) did not show any catalytic peak currents except for the rising non-catalytic currents in these two regions. CoPyPc has only one pronounced peak around II. On the other hand, MWCNT-COOH have no peak around II but a less pronounced peak around I. Lack of oxidation peaks for the bare GCE and MWCNT-COOH around II suggest that the peaks in this region are due to the redox couple of CoPyPc. Consequently, the CVs (Fig. 5.16B) were further obtained in pH 4 buffer solution in the absence of l-cysteine. Only surfaces containing CoPyPc showed peaks around II, Fig. 5.16B. Therefore, this is an indication that peaks around I are based on l-cysteine electrooxidation. SWV, Fig. 5.17, confirmed that the peak around I is due to l-cysteine since the current increased with concentration. The oxidation peak potential for linked nanocomposite is shifted to less potential values (as depicted by the dashed arrow in Fig. 5.16A), implying better electrocatalytic properties than the mixed nanocomposite. Lack of oxidation peak for the electrooxidation of l-cysteine on a bare GCE in pH 4 buffer within this potential window has been reported [120].

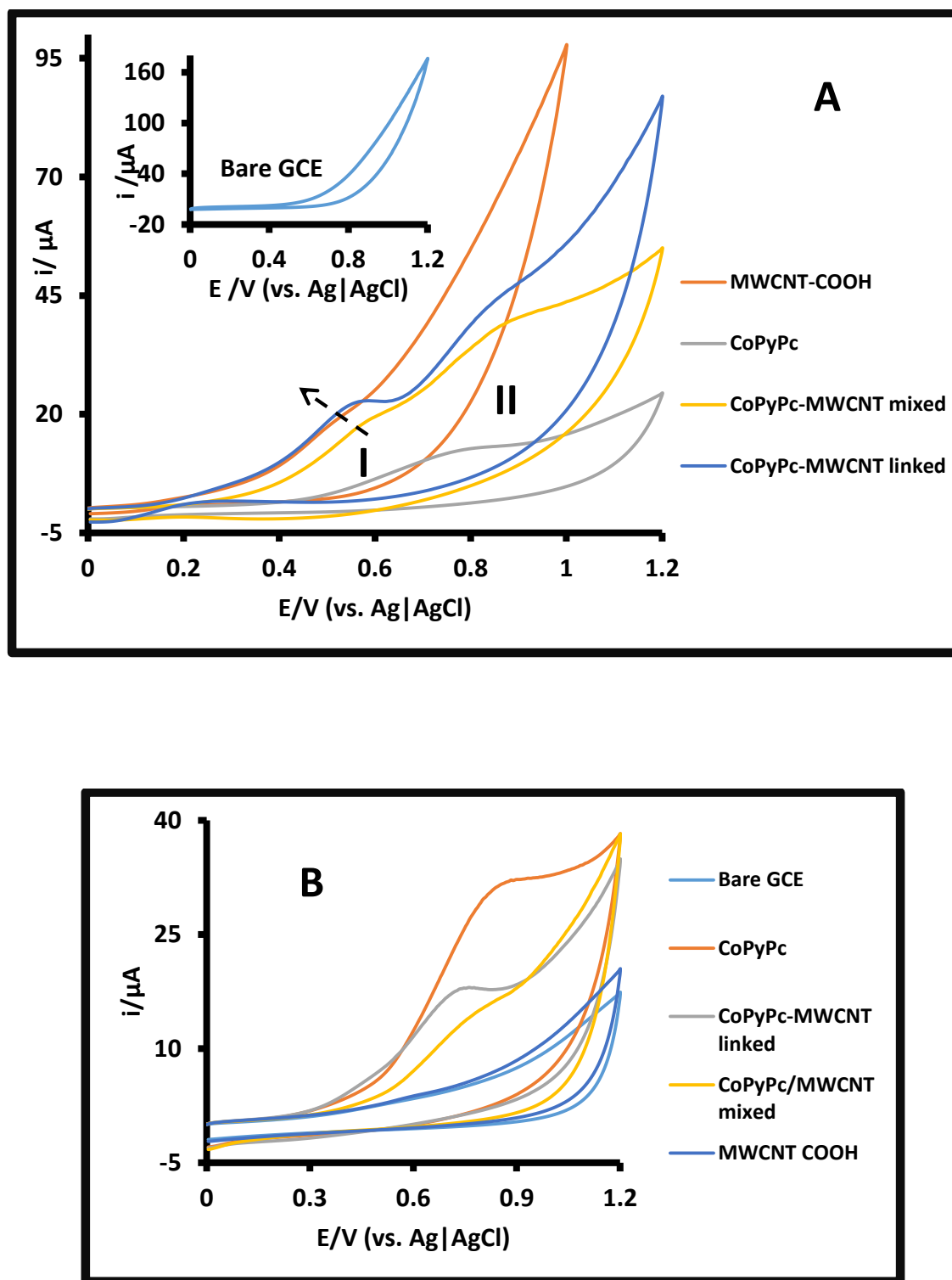


Fig. 5.16. (A) Cyclic voltammograms of 8 mM l-cysteine in pH 4 buffer solution using modified GCE surfaces. Inset = Bare GCE. (B) Cyclic voltammograms obtained in pH 4 buffer solution only using bare and modified GCE surfaces. Scan rate = 100 mV/s.

Voltammetric analysis techniques such SWV have been observed to be useful techniques for rapid and sensitive detection of analytes in electroanalytical applications. In this work, SWV was employed to gather data for the LOD of l-cysteine (Fig. 5.17, Inset = calibration curve). CoPyPc and CoPyPc-MWCNT (mixed) nanocomposite were not evaluated further since CVs proved they are inferior to the linked nanocomposite in terms of both oxidation potentials and peak currents, Fig. 5.16A.

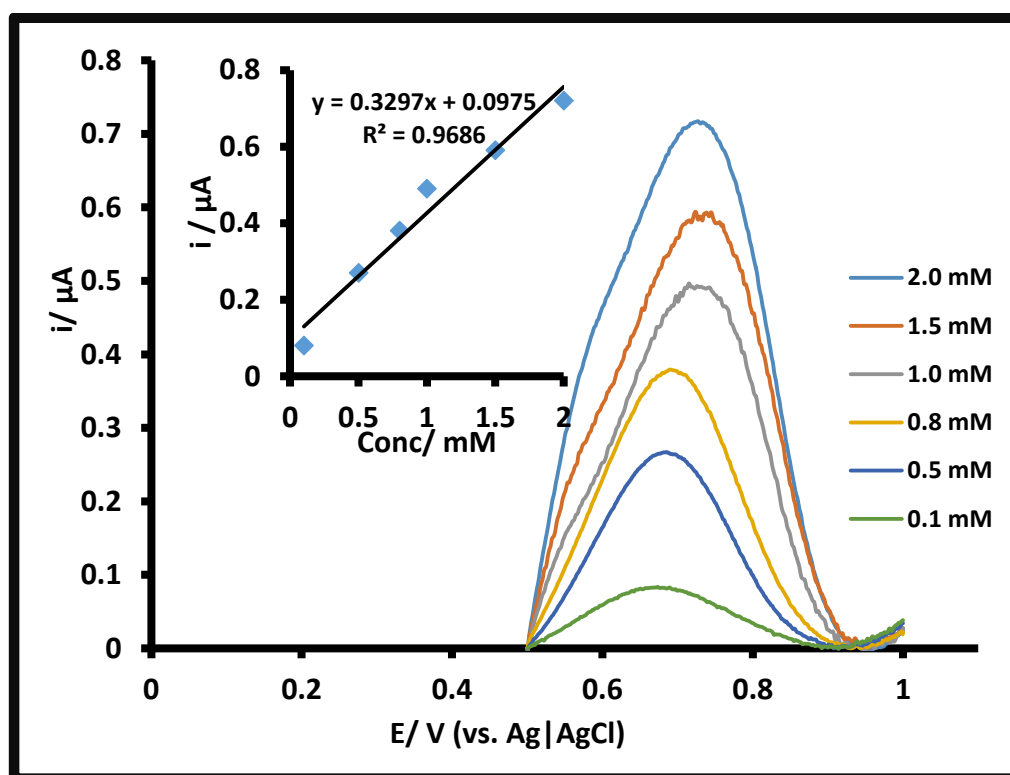


Fig. 5.17. Square wave voltammograms obtained for l-cysteine electrooxidation in pH 4 buffer using covalently linked CoPyPc-MWCNT modified GCE. Inset = Analytical calibration curve.

The LOD was then calculated using the 3σ -notation, and was found to be 2.96×10^{-7} M for the covalently linked CoPyPc-MWCNT nanocomposite, Tables 5.1 and 5.4. This LOD is well below the normal levels of common thiols in human beings [190]. Table 5.4 shows a comparison of the LOD in this work with other catalytic platforms applied for l-cysteine detection [191-197]. The lowest LOD was obtained for poly-electrode, and was much lower than reported in literature. Thus makes the poly-nanocomposite a potential tool for diagnosis of thiol-related diseases compared to other nanocomposites. Thus polymerisation is preferred for preparation of nanocomposite platforms for electrocatalysis, since better than sequential or mixed in terms of LOD, Table 5.4.

Table 5.4. Comparative LODs for the electrocatalysed oxidation of l-cysteine using different catalytic systems.

Electrode	pH	LOD	Ref.
GaN nanowires	7.4	0.5 μM	[191]
Pt nanoparticles/poly(o-aminophenol)-GCE	3.0	0.08 μM	[192]
Nafion/lead nitroprusside NPs-CCE	4.0	0.46 μM	[193]
BCNT-GCE.	7.4	0.26 μM	[194]
Pt/ CNT	7.4	0.3 μM	[195]
Layer-by-layer MWCNT-GCE	7.4	0.3 μM	[196]
CoOHETPc-SAM-Au	4.0	0.52 μM	[197]
FeOHETPc-SAM-Au	4.0	0.52 μM	[197]
CoPyPc-MWCNT-GCE (linked)	4.0	0.296 μM	TW
CoTAPc-MWCNT-GCE (mixed)	4.0	0.73 μM	TW
CoTAPc-MWCNT-GCE (sequential)	4.0	0.28 μM	TW
CoTAPc	4.0	1.24 μM	TW
Poly CoTAPc-MWCNT-GCE	4.0	0.017 μM	TW
Poly CoPyPc-MWCNT-GCE	4.0	0.036 μM	TW

NPs= nanoparticles, CCE= carbon ceramic electrode, BCNT= Boron-doped carbon nanotube, CNT= carbon nanotube, OHETPc= octa(hydroxyethylthio)-phthalocyanine, SAM= self-assembled monolayer, TW= This Work.

5.1.3.3. Chronoamperometry.

Repetitive chronoamperomograms for the linked nanocomposite are shown in Fig. 5.18. The catalytic activity of the linked and the mixed nanocomposites were weakly affected by the oxidation products. Although there was a significant current

decrease for both surfaces, the catalytic activities show current stability thereafter as depicted in Fig. 5.18. The ability to resist passivation is a crucial feature for materials destined for the fabrication of sensor platforms for routine analyses; this makes the linked and mixed nanocomposites to be suitable candidates for sensor development. Since the linked gave better current responses, this is more preferred than the mixed. Furthermore, it is well-known that the individual materials (MPc and MWCNT) are chemically and thermally stable [198,199] hence making these nanocomposites eligible for applications in which sterilization measures should be undertaken before reuse.

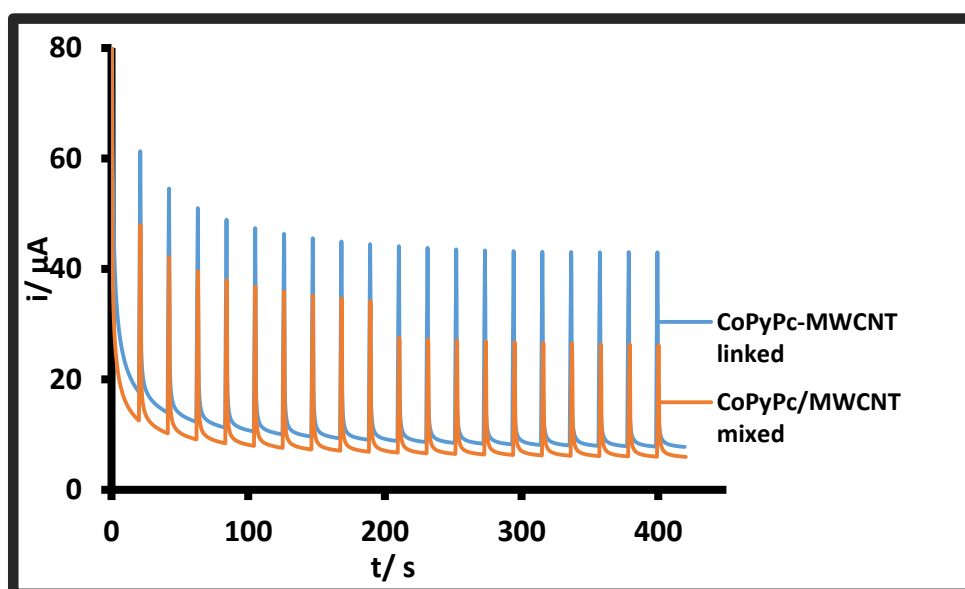


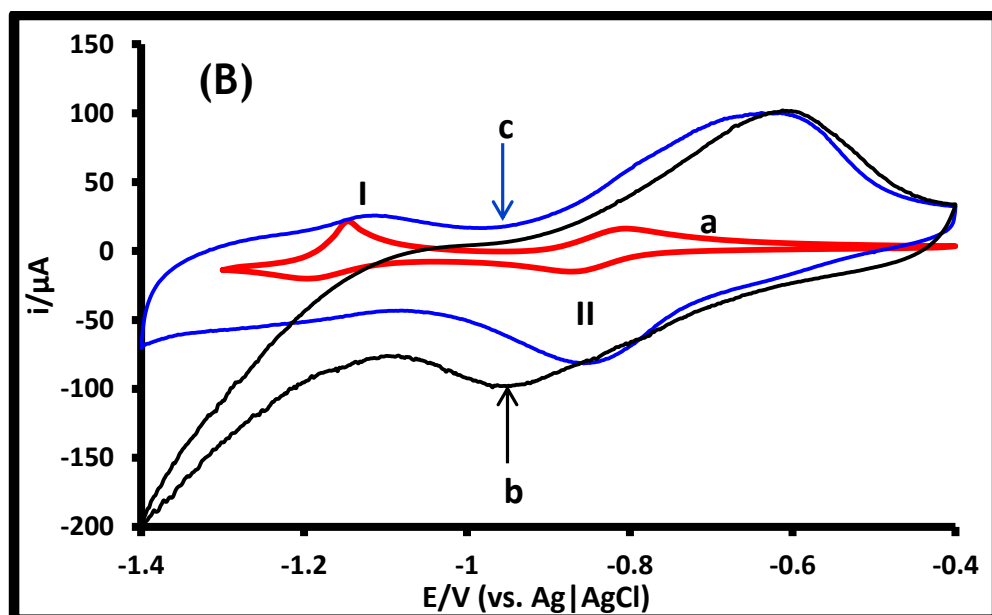
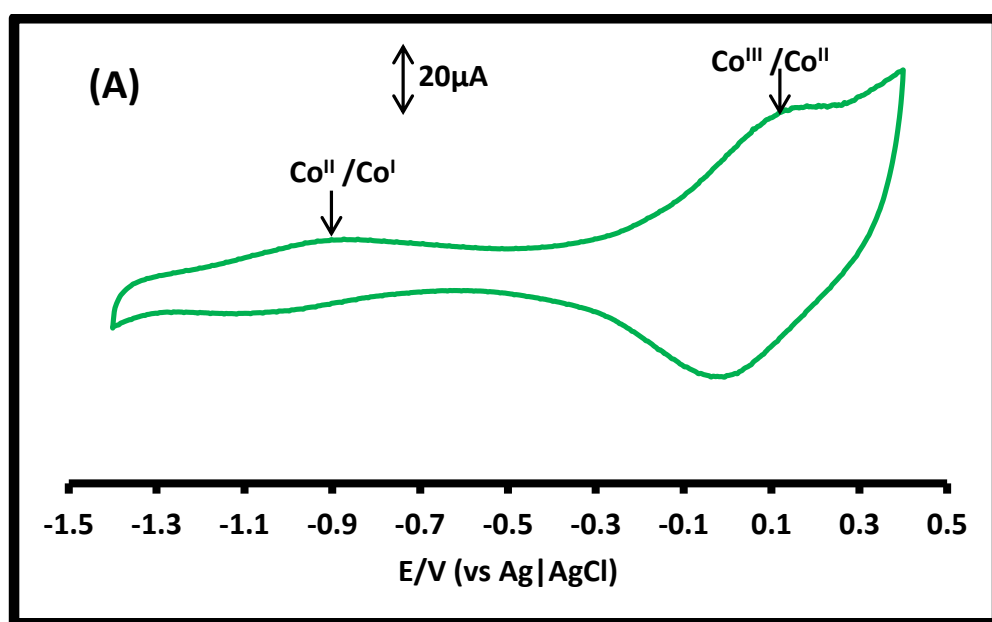
Fig. 5.18. Repetitive chronoamperograms (20 scans) in 20 mM l-cysteine in pH 4 buffer using covalently linked CoPyPc-MWCNT.

5.2. Paraquat.

5.2.1. CoTAPc (sequential) on MWCNT intercalated rGNS.

5.2.1.1. Cyclic Voltammetry.

The studies were done to examine the effectiveness of MWCNTs in separating rGNS for electroanalysis. PQ was used as an example.



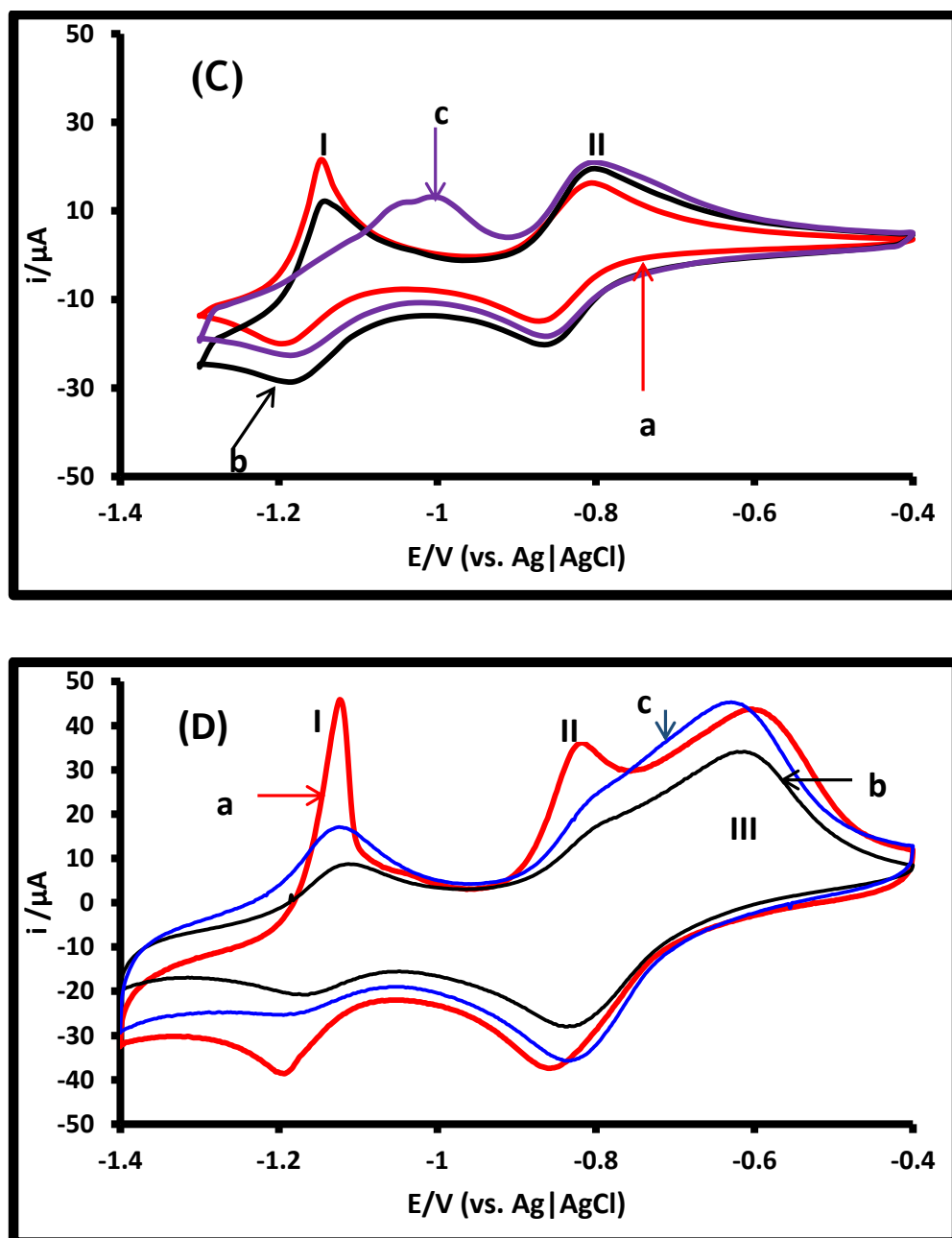


Fig.5.19. Second cycle Cyclic Voltammograms for (A) CoTAPc-rGNS-2-MWCNT-GCE in 0.1 M Na₂SO₄ electrolyte in the absence of PQ; (B) bare GCE (a), GONS-GCE (b) and CoTAPc-MWCNT-GCE (c); (C) bare GCE (a), rGNS- 2-GCE (b), rGNS-2-MWCNT-GCE (c); (D) CoTAPc-rGNS-2-MWCNT-GCE (a), CoTAPc-GCE (b), CoTAPc-rGNS-2-GCE (c), in 1 mM PQ in 0.1 M Na₂SO₄.

Fig. 5.19 shows the CV of CoTAPc-rGNS-2-MWCNT-GCE in the absence of PQ. There were no peaks observed with the bare GCE, rGNS-1-GCE and rGNS-2-GCE in the absence of PQ (figures are not shown). The peaks for CoTAPc-rGNS-2-MWCNT-GCE, Fig. 5.19A, are due to CoTAPc and are assigned to $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$ [19] and $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$, and these were also observed for CoTAPc-GCE, CoTAPc-rGNS-2-GCE and CoTAPc-MWCNT-GCE in the absence of PQ. The currents for PQ oxidation on GONS and MWCNT-CoTAPc were generally high, Fig. 5.19B, but the electron transfer performance for both were poor as the peaks potential separation were wide, Table 5.5.

The CoTAPc-MWCNT-GCE (mixed) and GONS-GCE were not probed any further for PQ reductions the sequential performed better for l-cysteine above. rGNS-1-GCE was also not probed further in the presence of PQ since its performance in $\text{Fe}(\text{CN})_6^{3-/4-}$ was inferior to rGNS-2 and the latter allows to see the effects of CoTAPc. There are two prominent redox processes for PQ reduction on bare-GCE, rGNS-2-GCE, rGNS-2-MWCNT-GCE (Fig. 5.19C); CoTAPc-GCE, CoTAPc-rGNS-2-GCE and CoTAPc-rGNS-2-MWCNT-GCE (Fig. 5.19D) indicated as (I) and (II) on the CVs and listed in Table 5.5. The peak potentials do not vary much from each other on the different electrodes. The first reduction process (II) is not well defined for CoTAPc-GCE and CoTAPc-rGNS-2-GCE, it appears as a shoulder to the process (III) (due to $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$), making PQ analysis using the process difficult for these electrodes. However, process (I) is more resolved for PQ reduction on both CoTAPc-GCE and rGNS-2-CoTAPc-GCE.

Table 5.5. A summary of some electrochemical properties for the different CoTAPc electrode surfaces.

Electrode surface	Half wave potential for PQ/ (V) Peak (i) ^d	Half wave potential for PQ/ (V) Peak (ii) ^d	k_{ET} /s
Bare GCE	-1.17, (0.05)	-0.84 (0.07)	1.62
GONS-GCE	--- ^a	-0.79 (-0.34)	--- ^b
rGNS-2-GCE	-1.16 (0.07)	-0.83 (0.05)	1.36
rGNS-2-MWCNT-GCE (mixed)	-1.11 (0.13)	-0.83 (0.05)	2.01
CoTAPc-GCE	-1.11 (0.02)	-0.82 ^c	--- ^b
rGNS-2-CoTAPc-GCE (sequential)	-1.16 (0.08)	-0.82 ^c	--- ^b
MWCNT-CoTAPc-GCE (sequential)	-1.16 (0.08)	---- ^b	--- ^b
rGNS-2-MWCNT-CoTAPc-GCE (sequential)	-1.17 (0.08)	-0.82 (0.04)	2.12

^a no peak, ^bFirst reduction peak was not well resolved, ^c Peak potential not half-wave potential, ^dValues in brackets are ΔE .

It is however preferable to use lower potentials for analytical purposes. Both processes (I) and (II) are resolved for PQ reduction on CoTAPc-rGNS-2-MWCNT-GCE. Hence CoTAPc-rGNS-2-MWCNT-GCE has more advantage compared to other electrodes containing CoTAPc. CoTAPc-GCE and CoTAPc-rGNS-2-GCE will not be

considered further since the first reduction is not resolved. The two reduction processes for PQ (labelled as I and II) are assigned PQ^{2+} to PQ^+ and PQ^+ to PQ^0 reductions, respectively. Process (III) occurs only in the presence of CoTAPc and it is in the potential range for Co^{II}/Co^I in CoTAPc [19], shifted to less negative values in the presence of PQ compared to Fig. 5.19A (in the absence of PQ). This process is in the potential range for PQ reduction, and hence it is involved in the catalysis of PQ. Surface fouling tests on the modified electrodes for PQ detection were performed by running continuous CVs (90 cycles) in PQ solution (figures not shown). There was no significant change in the voltammograms showing no sign of fouling.

5.2.1.2. SECM.

SECM approach curves and 3D-SECM images were used to probe into the surface reactivity and topography of the modified surfaces. From the approach curves (Fig. 5.20A), the reduced graphene nanocomposites show a conducting behaviour (curves b, c, d, e, f and g) whereas the GONS show insulating properties (curves (a) and (h)) in both ferrocyanide and PQ redox solutions, even though GONS showed some CV peaks in PQ solution, Fig. 5.19B. The superior behaviour of CoTAPc-rGNS-2-MWCNT-GCE is also observed using SECM approach curves, Fig. 5.20, showing larger currents.

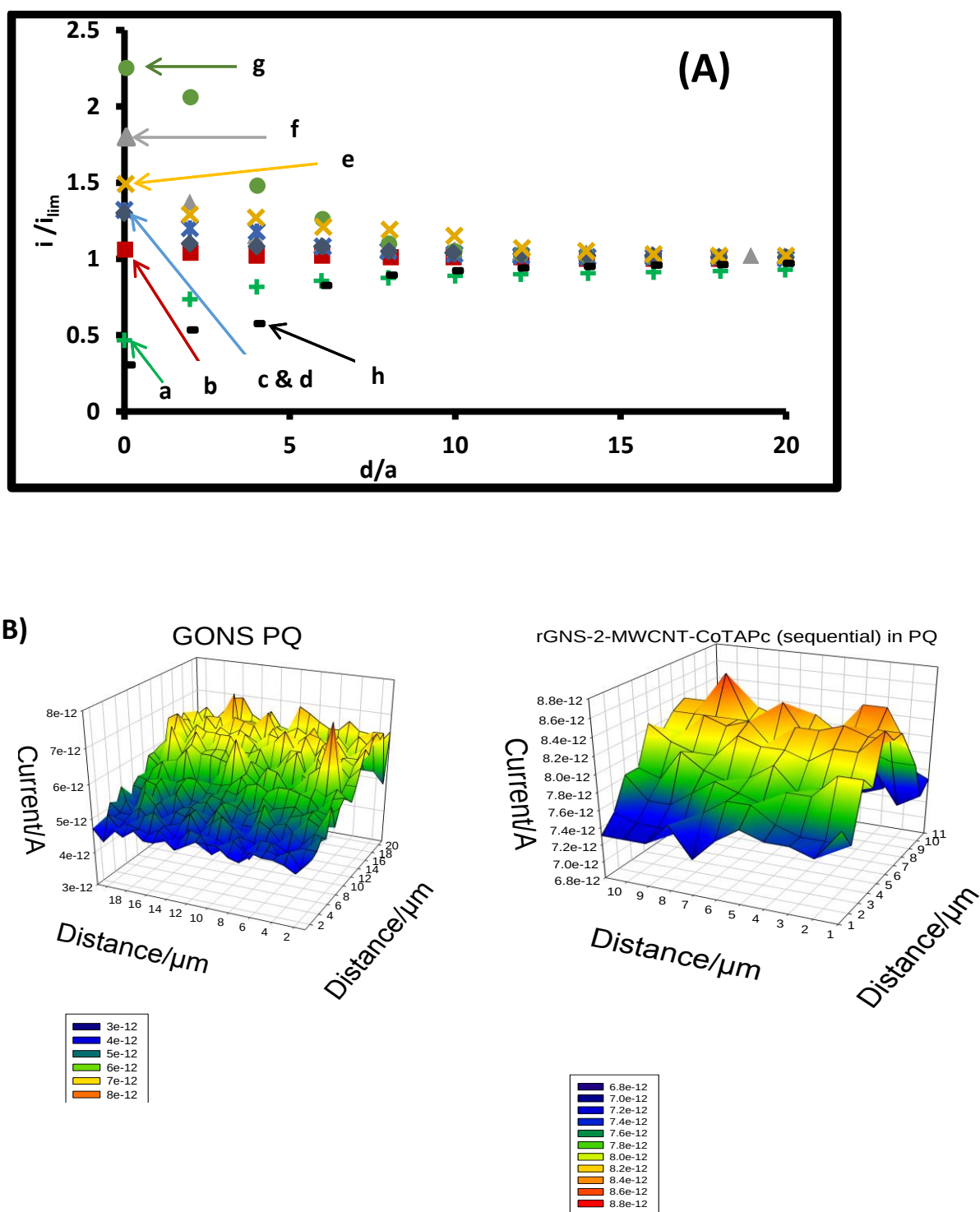


Fig. 5.20. (A) SECM approach curves for GONS (a), CoTAPc (b), rGNS-2 (c), rGNS-2-MWCNT (mixed) (d), rGNS-2-CoTAPc (sequential) (e), CoTAPc-MWCNT (sequential) (f), CoTAPc-rGNS-2-MWCNT (sequential) (g), and GONS (h). (a-g) were performed using 1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl, and (h) was obtained using 1 mM PQ in 1M Na_2SO_4 . (B) SECM images for GONS and CoTAPc-rGNS-2-MWCNT obtained using 1 mM PQ in 1 M Na_2SO_4 . UME = 10 μm . All on glassy carbon plates.

The trend in activity as revealed by the calculated tip current-limiting current ratios (i/i_{lim}) is as follows; CoTAPc (1.06) < rGNS-2 (1.30) ~ rGNS-2-MWCNT (1.30) < CoTAPc-rGNS-2 < (1.49) CoTAPc-MWCNT (1.80) < CoTAPc-rGNS-2-MWCNT (2.25). This is further confirmation that CoTAPc-rGNS-2-MWCNT has superior properties relative to other nanocomposites studied in this work. The 3D-SECM mesh plots (Fig. 5.20B) were used to reveal surface topography. GONS surface is rougher as compared to CoTAPc-rGNS-2-MWCNT nanocomposite in the presence of PQ. This may result in a higher surface area for the former being exposed to the redox couple, hence the observed high cyclic voltammetry currents in Fig. 5.19B. However, because of the defects in GONS, there is slow electron transfer as demonstrated by a wide peak potential separation.

5.2.1.3. Kinetics and LODs for PQ detection.

To confirm if there is absence or presence of chemical complications during the detection of PQ for the remaining electrodes: bare GCE, rGNS-2, rGNS-2-MWCNT and CoTAPc-rGNS-2-MWCNT-GCE, a graph of $\frac{I}{v^{1/2}C}$ vs. v was plotted as shown in Fig. 5.21.

The shapes of the curves for modified surfaces suggest the coupling of an electron transfer process by a chemical process. This can also imply a possibility of a catalytic process. The absence of a chemical complication is shown by a nearly horizontal line [200] as observed with the bare GCE (slope; 0.00002, R^2 ; 0.88). CoTAPc-rGNS-2-MWCNT-GCE surface showed a larger exponential decay with increase in scan rate than all other surfaces, Fig. 5.21. The plots in Fig. 5.22 were used to confirm if PQ adsorbed onto the electrode surface during its detection on our sensor platform.

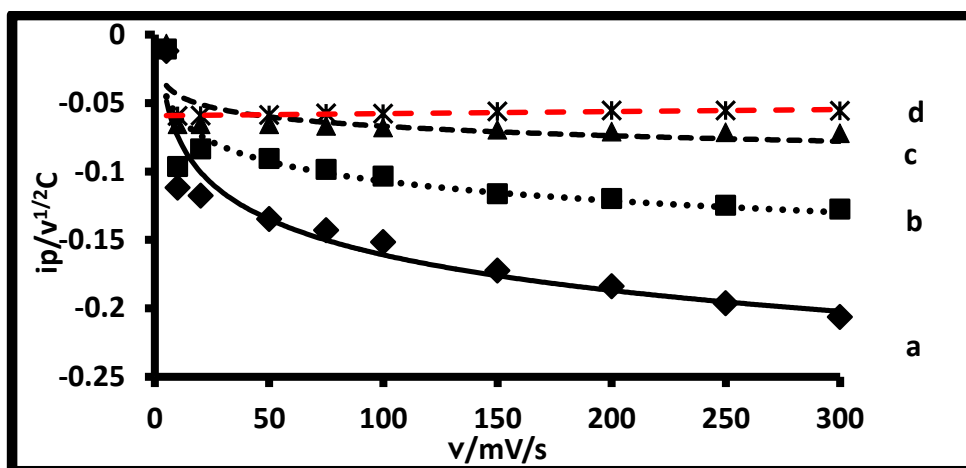


Fig. 5.21. Plots of $\frac{i_p}{v^{1/2}}$ vs v for CoTAPc-rGNS-2-MWCNT-GCE (a), rGNS-2-MWCNT-GCE (b), rGNS-2-GCE (c), and Bare GCE (d).

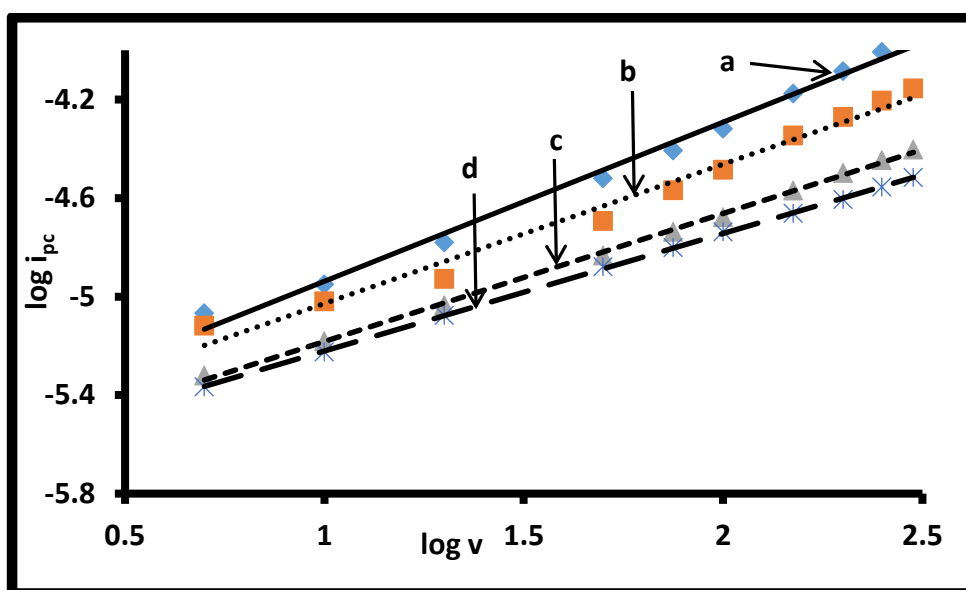


Fig. 5.22. Plots of $\log(i_{pc})$ vs. $\log(v)$ for CoTAPc-rGNS-2-MWCNT-GCE (sequential) (a), rGNS-2-MWCNT-GCE (mixed) (b), rGNS-2-GCE (c) and bare GCE in the presence of 1 mM PQ in 0.1 M Na_2SO_4 electrolyte.

For adsorbed species, the theoretical value for the slope from plots of log current versus log scan rate is 1.0. The slope is 0.50 for a diffusion-controlled mechanism.

The values of slope obtained for CoTAPc-rGNS-2-MWCNT-GCE, rGNS-2-MWCNT-GCE, rGNS-2-GCE and GCE are 0.65, 0.57 and 0.52, 0.48, respectively. These slopes were obtained using cathodic peak currents. The values of the slopes (except for bare) are above 0.5 indicating an adsorption process during PQ detection on graphene platforms. Thus adsorption is involved during PQ detection. The CoTAPc-rGNS-2-MWCNT-GCE showed the highest slope value (0.65) in Fig. 5.22, hence more PQ adsorption on this modified surface. The slopes of log current versus log scan rate values are closer to 0.5 than to 1, showing combined diffusion and adsorption controlled. However, the Laviron equation (for adsorbed species), Eq. 5.4, [201,202] was employed for comparative purposes and the values of the electron transfer rate constants (k_{ET}) obtained are estimates.

$$\log k_{ET} = \alpha \log(1-\alpha) + (1-\alpha) \log \alpha - \log \left(\frac{RT}{nFv} \right) - \alpha(1-\alpha) \frac{nF\eta}{2.3RT} \quad (5.4)$$

where η is the overpotential, v is the scan rate, n the number of electrons involved, T and R have their usual meanings. The Laviron method relies on the transfer coefficient (α), which is a measure of the symmetry of the energy barrier of the redox reaction. α is expected to be = 0.5. However in many cases α deviates from 0.5. α is determined from the plot of E_p vs. $\log v$ [202] for both cathodic and anodic peaks. The slope of the straight line plot is given in Eq. 5.5, which is $b/2$ in Eq.5.1.

$$\text{Slope} = \frac{2.3RT}{\alpha nF} \quad (5.5)$$

Using the α value determined in equation 5.5, equation 5.4 was then employed to determine the k_{ET} values. The calculated rate constants changed significantly upon addition of MWCNT (compare rGNS-2-GCE ($k_{ET} = 1.36 \text{ s}^{-1}$) and rGNS-2-MWCNT-GCE

($k_{ET} = 2.01 \text{ s}^{-1}$), Table 5.5. This implies that addition of MWCNT improves not only results in separation of the graphene nanosheets but also electron transfer properties. The value for the bare GCE is $k_{ET} = 1.62 \text{ s}^{-1}$. k_{ET} value is the highest for CoTAPc-rGNS-2-MWCNT-GCE at 2.12 s^{-1} , showing its superior electron transfer properties. As such this electrode was employed for the determination of detection limits.

5.2.1.4. SWV.

The LOD was investigated through SWV studies, and the results are presented in Fig. 5.23. This was only done for the best electrode i.e. CoTAPc-MWCNT-rGNS-2.

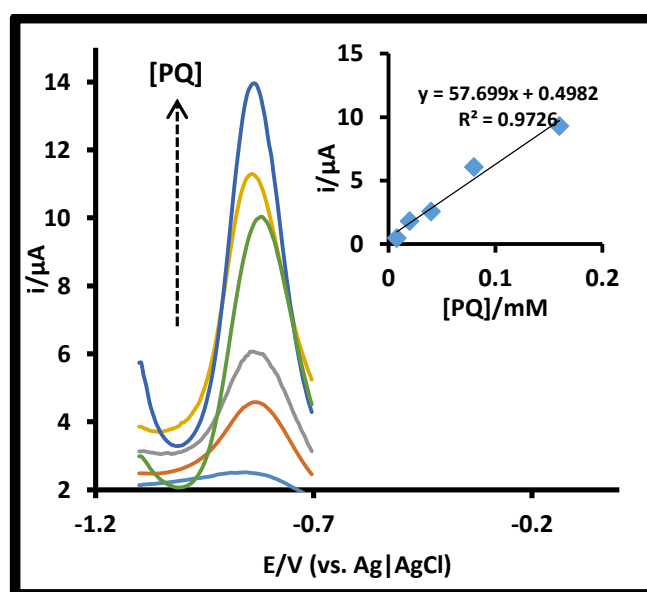
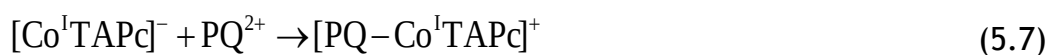


Fig. 5.23. Square Wave voltammograms of CoTAPc-MWCNT-rGNS-2 nanocomposite toward different concentration of PQ in Na_2SO_4 electrolyte. The insert shows the analytical curve.

The LOD was calculated using the 3σ -notation [203-205], where σ is the standard deviation and 3 is a recommended factor that gives a practical confidence of 90% to

99.7%. Taking into consideration the sensitivity of the analytical curve, the LOD in this work was found to be 3.32×10^{-8} M using the anodic peak on CoTAPc-rGNS-2-MWCNT-GCE. A LOD of the order of 10^{-7} M has been reported when using a related phthalocyanine-based pyrolytic graphite electrode [206]. The Interim Maximum Acceptable Concentration (IMAC) for PQ as a dichloride in drinking water is 10 µg/L (3.88×10^{-8} M) [207], which is higher than that reported here for CoTAPc-rGNS-2-MWCNT-GCE. This makes the nanocomposite a feasible architecture for monitoring herbicides such as PQ in water bodies. As stated above Co(I)TAPc catalyses the reduction, hence the first step is the reduction of Co(II)TAPc to Co(I)TAPc, (eq 5.6), followed by adsorption of PQ (eq 5.7) and its reduction (eq 5.8).



PQ^+ would then be reduced further, resulting in two cyclic voltammetry peaks.

5.2.1.5. Selectivity studies on detection of PQ.

The suitability of a nanocomposite for sensor development is governed by its tolerance to competing interferences within the matrix. Some major agrochemicals that are widely used in both agricultural and non-agricultural activities i.e. amitrole, diuron, atrazine and urea, have been selected for this particular study. These agrochemicals are likely to be found coexisting with PQ in environmental waters and as such it is of paramount importance to investigate their interference effect on PQ

detection. The mixed solution method [208] using amitrole, diuron, atrazine and urea as interferents, was used to investigate the selectivity of the CoTAPc-rGNS-2-MWCNT modified GCE. Equation 5.9 was used to determine values of the selectivity coefficients (K_{amp}). K_{amp} gives a measure of the degree of interference.

$$K_{amp} = \left(\frac{I_{mixture}}{I_{PQ}} - 1 \right) \frac{[PQ]}{[Interferent]} \quad (5.9)$$

where $I_{mixture}$ and I_{PQ} are background corrected current responses of PQ in the presence and absence of the interferent, respectively, and $[PQ] = [Interferent] = 30 \mu\text{M}$.

K_{amp} value in the order of magnitude higher than 10^{-3} indicates strong interference and a value close to 10^{-3} indicates weak interference. A K_{amp} value of 8.3×10^{-3} was obtained for diuron. This shows that diuron has only a weak interference towards detection of PQ. Atrazine, amitrole and urea gave K_{amp} values of 2.98×10^{-1} , 2.5×10^{-2} and 7.5×10^{-2} , respectively. Such values show that these two agrochemicals have strong interference effect on PQ detection. Therefore this sensor platform can be applied without any pre-separation procedures for the determination of PQ in the presence of diuron. However its detection in the presence of atrazine, amitrole and urea, should be preceded by pretreatment.

5.3. ORR Studies.

5.3.1. rGNS-2-CdSe-QDs-CoPyPc (sequential) nanocomposites.

5.3.1.1. Cyclic Voltammetry.

The studies were done to check the effect of QDs in separating rGNS-2 using ORR as an example. To gain insight into the ORR electrochemical activity by the bare GCE and the modified surfaces, cyclic voltammetry was performed in air saturated 0.5 M NaOH electrolyte, Fig. 5.24. ORR activity was clearly observed with the rGNS-2-CdSe QDs, CoPyPc, CoPyPc-rGNS-2-CdSe-QDs), CoPyPc-rGNS-2, and bare. No clear ORR peaks were observed with rGNS and CdSe QDs alone. CoPyPc-rGNS-2-CdSe-QDs showed slightly more favourable reduction potential compared to CoPyPc-rGNS-2, Table 5.6. Furthermore, the onset reduction potential for both CoPyPc-rGNS-2 and CoPyPc-rGNS-2-CdSe-QDs were the least negative in this study (i.e. -0.34 V and -0.31 V, respectively), making them potential nanocomposites for ORR activity, Table 5.6. It is important to note that CoPyPc-rGNS-2-CdSe-QDs is still superior to CoPyPc-rGNS-2 in terms of peak potentials.

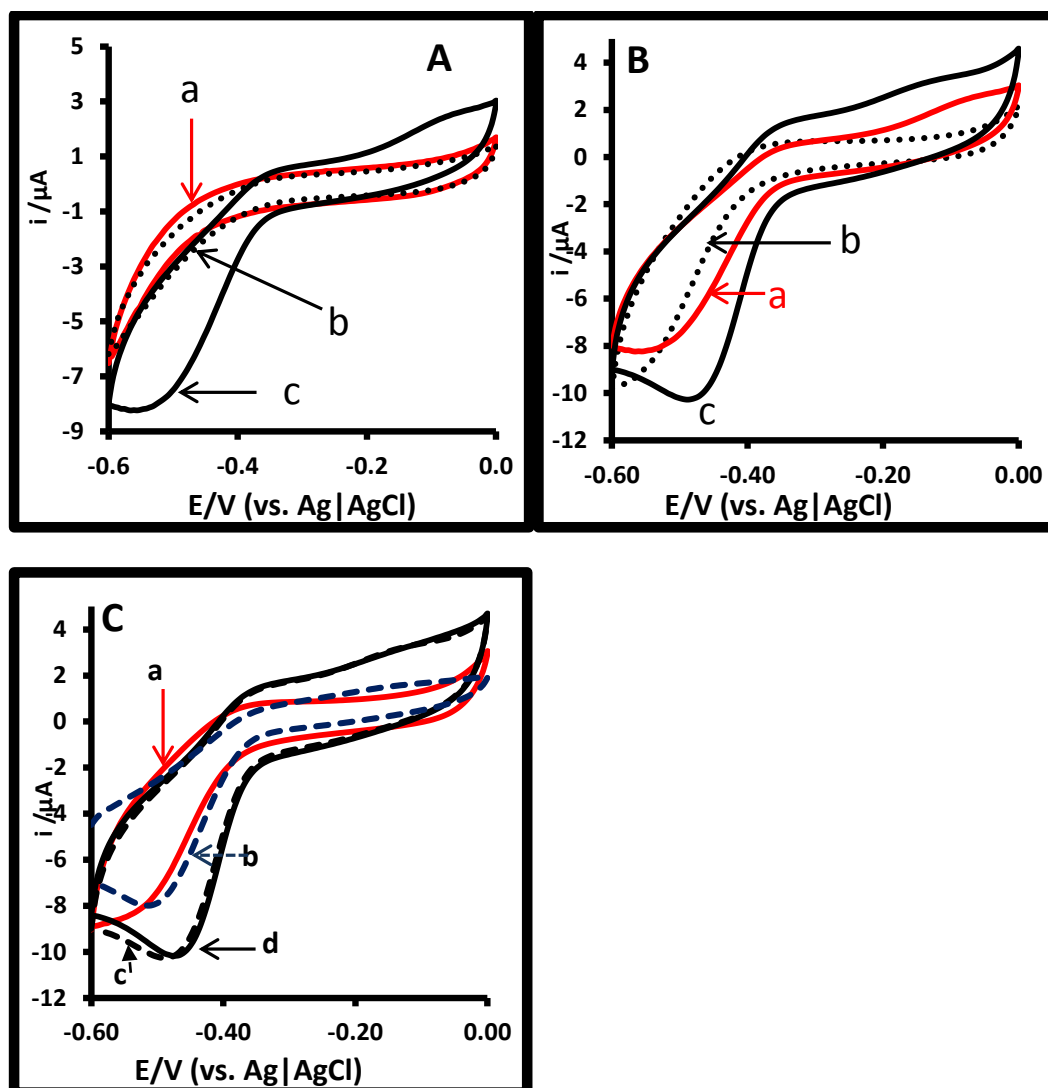


Fig. 5.24. (A) CVs for the ORR using CdSe-QDs (a), rGNS-2 (b), rGNS-2-CdSe-QDs (mixed) (c); (B) rGNS-2-CdSe-QDs (mixed) (a), bare (b) and CoPyPc-rGNS-2 (sequential) (c); (C) CoPyPc (a), CoPyPc-CdSe-QDs (sequential) (b) CoPyPc-rGNS-2 (sequential) (c) and rGNS-2-CdSe-QDs-CoPyPc (sequential) (d) in air saturated 0.5 M NaOH, scan rate = 100mV/s.

The reduction catalytic currents were also higher for both CoPyPc-rGNS-2-CdSe-QDs and CoPyPc-rGNS-2. The results show that reduced graphene nanosheets promote the electrocatalytic behaviour of CoPyPc. The enhancement in currents (for both CoPyPc-rGNS-2 and CoPyPc-rGNS-2-CdSe-QDs) and the less negative potential (for CoPyPc-rGNS-2-CdSe-QDs) show the need for reducing graphene oxide and adding

intercalating agents to improve on electron transfer kinetics, and consequently better ORR electrocatalytic performance.

Table 5.6. ORR reduction potentials using different electrocatalysts.

Electrodes	E/ V (ORR)/ vs. Ag AgCl (3 M KCl).	ORR onset potential/ V
CdSe	---a	---a
rGNS-2	---a	---a
CoPc	-0.48	-0.37
Iodine Doped CoPc	-0.48	-0.35
CoPyPc	-0.53	-0.37
CoPyPc-rGNS-2 (sequential)	-0.48	-0.34
rGNS-2-CdSe-QDs (mixed)	-0.55	-0.36
CoPyPc-CdSe-QDs (sequential)	-0.52	-0.36
CoPyPc-rGNS-2-CdSe-QDs (sequential)	-0.46	-0.31
Iodine doped CoPyPc-MWCNTs (sequential)	-0.45	-0.33
Iodine doped CoPyPc	-0.42	-0.31
CoPyPc-MWCNTs (sequential)	-0.41	-0.31
MWCNTs	-0.52	-0.42
Bare GCE	-0.49	-0.38

a = no defined peaks.

5.3.1.2. RDE Studies.

The kinetics of ORR on the CoPyPc-rGNS-2-CdSe-QDs was further probed using the RDE hydrodynamics. Typical stationary current-potential curves obtained at different rotation rates are shown in Fig. 5.25.

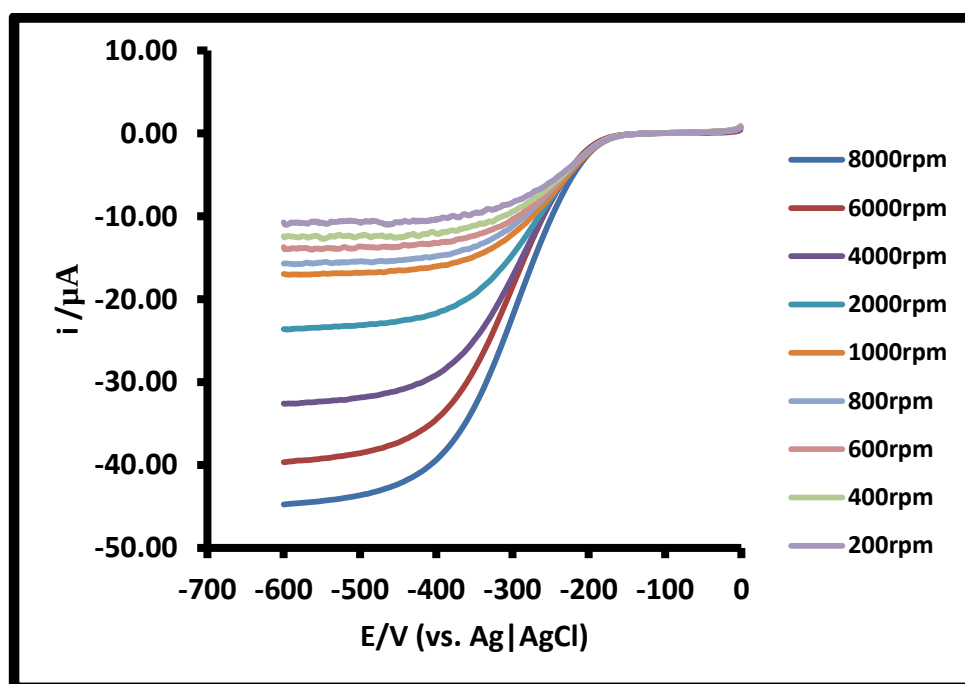


Fig. 5.25. Linear sweep voltammograms for ORR in air saturated 1.0 M NaOH on a CoPyPc-rGNS-2-CdSe-QD rotating disk electrode at different rotating rates. Scan rate: 1 mV/s.

Typical diffusion plateau-like waves are observed. Linear correlations (using Levich Equation 4.3) were obtained indicating diffusion-controlled mass transport.

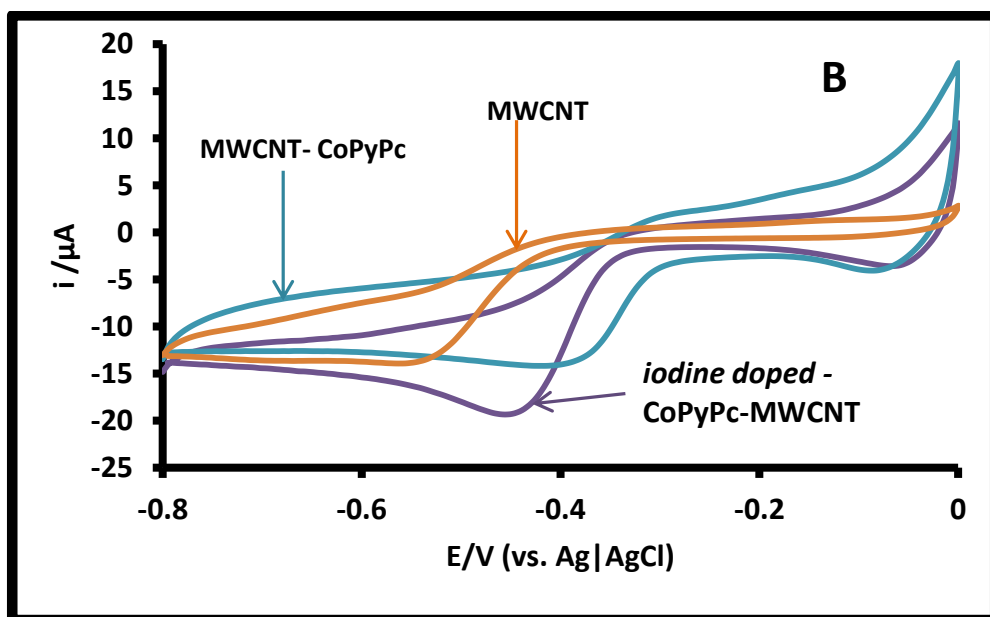
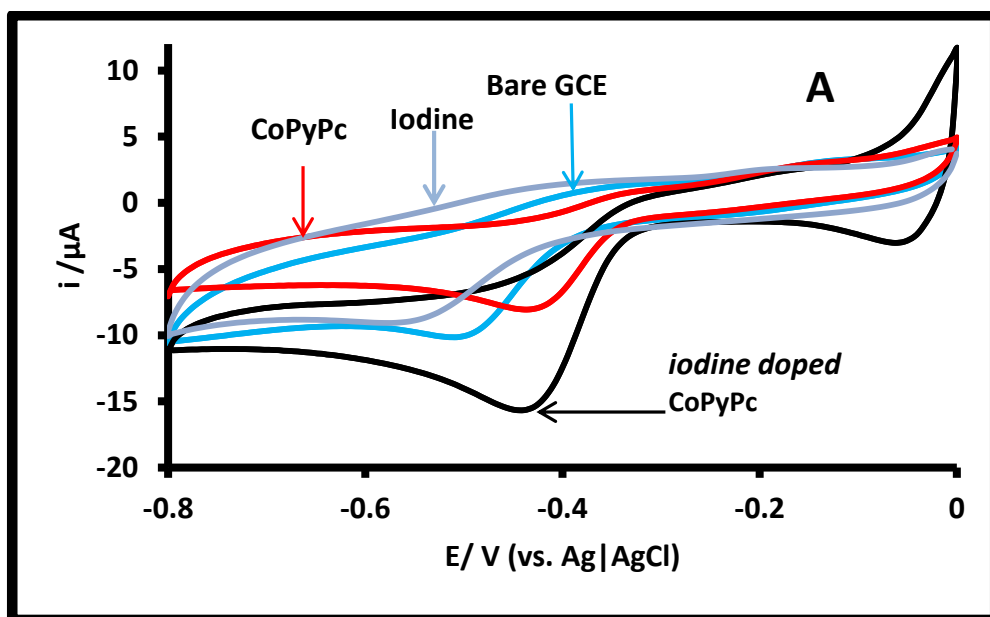
The Koutecky-Levich data used to calculate the number of electrons transferred for ORR were obtained from the experimental data shown in Fig. 5.25. The numbers of electrons transferred were found to be 3.5, which is close to 4, typical for oxygen

reduction in basic media. The preferred ORR is when $n = 4$ which results in production of water than when $n = 2$ which gives out hydrogen peroxide.

5.3.2. Iodine doped CoPyPc.

CV technique, Fig. 5.26, was used to elucidate the electrochemical response of the ORR catalysed by surface adsorbed catalysts. The onset potential and peak currents demonstrate the catalytic activity of a catalyst. All the adsorbed species on the electrode surface demonstrated ORR electrocatalysis. However the adsorbed species show different onset potentials. An earlier onset potential demonstrates better ORR electrocatalytic activity. The onset potentials were the same for iodine doped-CoPyPc, CoPyPc-MWCNT and CoPyPc-rGNS-2-CdSe-QDs at -0.31 V, Table 5.6.

ORR onset potential on iodine doped-CoPyPc-MWCNT slightly shifted to a more negative value of -0.33 V, however the peak currents were more pronounced for iodine doped CoPyPc-MWCNT ($\approx 20 \mu\text{A}$), Fig. 5.26B, relative to all other adsorbed species in this work ($\leq 15 \mu\text{A}$), Fig. 5.26A and B. There was poor performance observed for the bare GCE and MWCNT-GCE in terms of both onset potentials and catalytic peak currents. Low peak currents at more negative potentials mean that the current density is low for the bare GCE and MWCNT alone. This makes the iodine doped-CoPyPc-MWCNT nanocomposite a better platform for ORR electrocatalysis in terms of enhanced currents. GCE was also modified with I_2 and ORR activity tested. The onset and ORR peak potentials were more negative (at -0.42 V) than for the bare GCE, Fig. 5.26A.



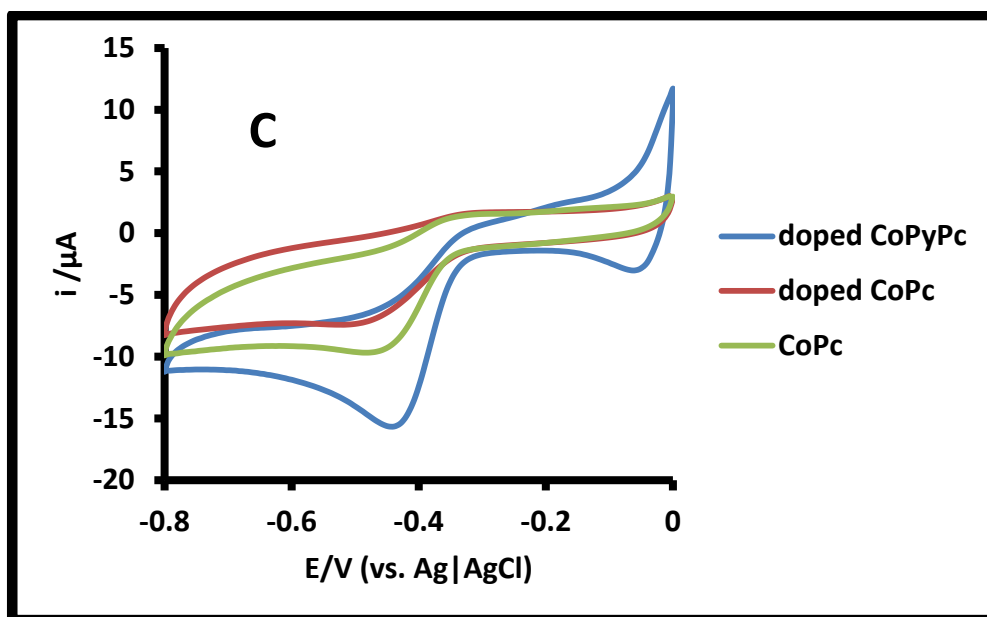


Fig. 5.26 (A-C). CVs for the ORR using the bare and modified electrodes in air saturated 0.5 M NaOH, scan rate = 100 mV/s.

The signal obtained for iodine modified GCE (Fig. 5.26A) is attributed to bare GCE and the shift of ORR peak to more negative potentials indicates partial passivation of the bare GCE with residual iodine. Unsubstituted doped and undoped CoPc did not show any significant distinction in terms of ORR peak (at -0.48 V) potentials but a reduction in onset potential was observed upon doping, Table 5.6. Furthermore, a clear distinction was observed relative to doped CoPyPc, Fig. 5.26C, signifying the necessity of ring substitution before successful doping. Although the onset potentials observed in this work are slightly more negative than observed for Pt-catalysts, it has been demonstrated in this work that CoPyPc is resistant to methanol crossover effect to be discussed later. Besides being very expensive the Pt-catalysts have been reported to suffer severely from methanol crossover effect resulting in serious

sluggish reaction [107]. The ORR peaks shifted towards negative potentials with scan rate as shown in Fig. 5.27.

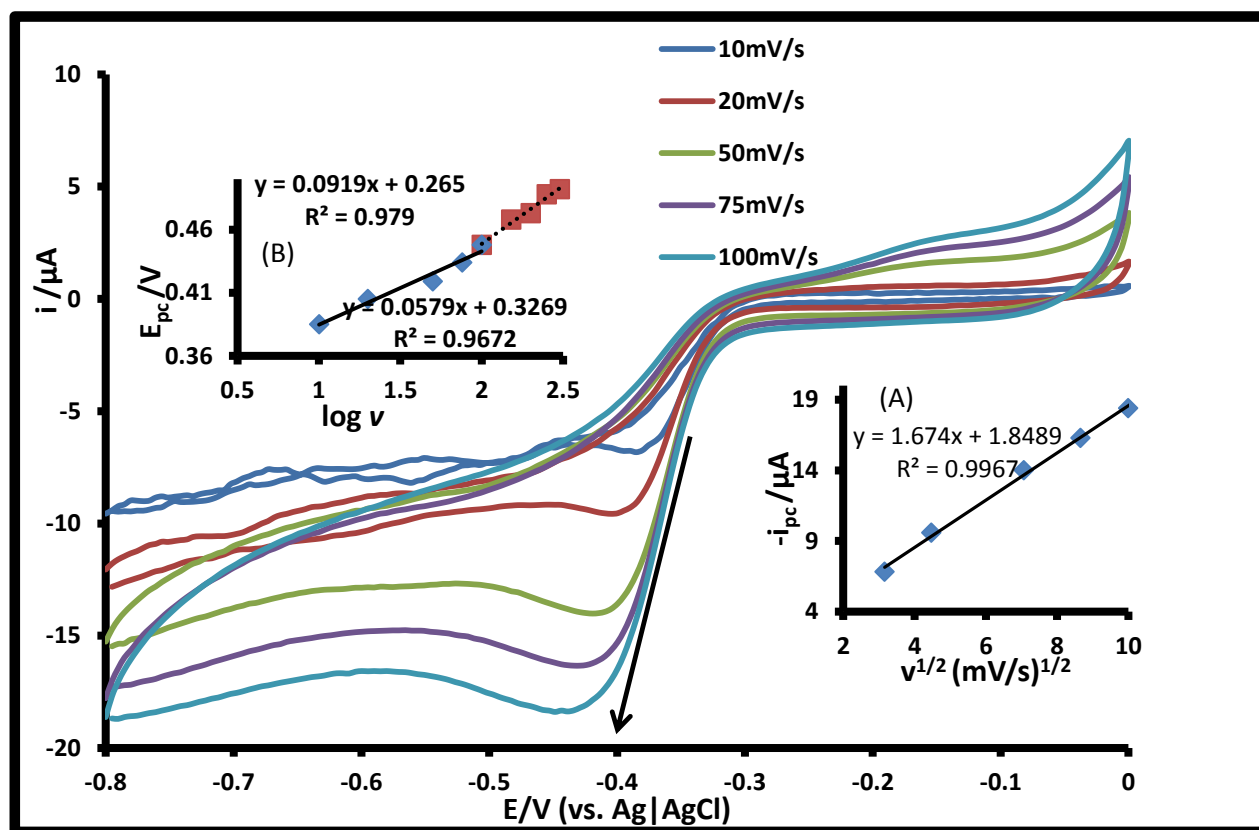
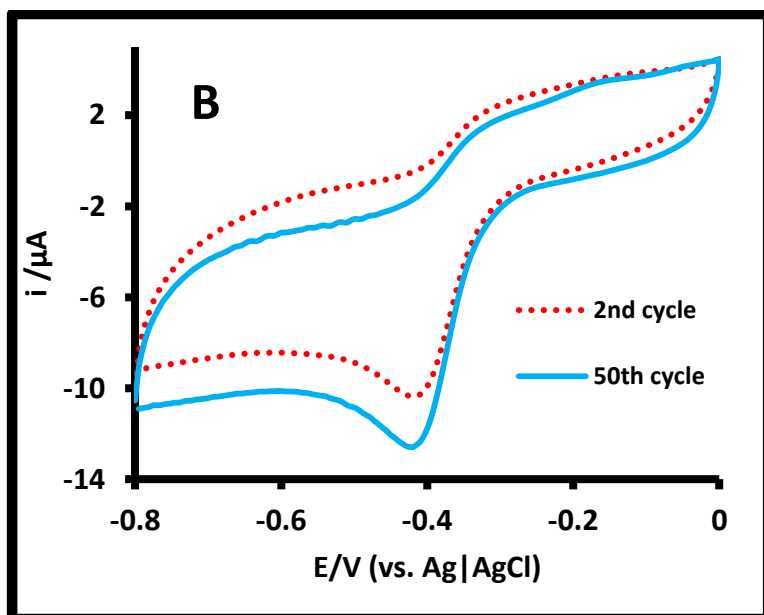
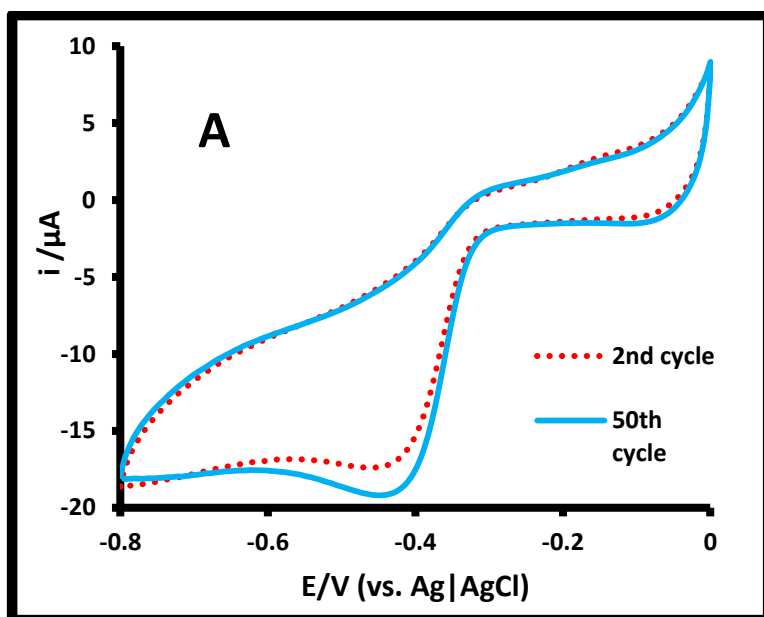


Fig. 5.27. CVs showing the effect of scan rate on ORR using iodine doped-CoPyPc-MWCNT nanocomposite in air saturated 0.5 M NaOH. Insert A = A plot of i_{pc} vs. $v^{1/2}$. Insert (B) = plot of peak potential vs. log scan rate.

This is an indication of irreversibility of the redox reaction. A plot of i_{pc} vs. $v^{1/2}$ was linear (Fig. 5.27 inset A), an indication of a diffusion controlled reaction at the surface of the adsorbed nanocomposite.

The Tafel slope was only calculated for the iodine doped CoPyPc-MWCNT nanocomposite since it proved to be more superior to other nanocomposites with respect to their catalytic currents. The Tafel slope was determined from Equation 5.1.

Two Tafel slopes were obtained as shown in Fig. 5.27 inset B. Tafel slopes (2 x slope of E_p vs. $\log v$ plot) were found to be 115.8 mV/decade at lower $\log v$ values, and 183.8 mV/decade at higher $\log v$ values. The presence of two Tafel slopes has also been observed before [209,210]. A value close to 120 mV/dec implies that the first electron transfer is the rate determining step. The higher Tafel slope than expected can be attributed to slow O_2 adsorption step becoming the rate limiting step at higher overpotentials or can be explained in terms of surface blockage of the reaction surface with ORR intermediates such as H_2O_2 . A low Tafel slope showing high current densities at low potentials has also been observed for an oxygen evolution reaction [211]. It is therefore imperative for an electrochemical reaction to exhibit a low Tafel slope so that it gains a high current density at low overpotential. This makes the iodine doped-CoPyPc-MWCNT nanocomposite a promising candidate for ORR. This nanocomposite is also electrochemically stable in the presence of oxygen as shown in Fig. 5.28A. Infact, the 50th cycle gained more catalytic currents than the second cycle upon repetitive cyclisation. The same behaviour was also observed for undoped-CoPyPc-MWNCT (Fig. 5.28B). However, the ORR catalytic currents for the undoped-CoPyPc-MWNCT nanocomposite were less than the doped nanocomposite. Figs. 5.28C and D show stabilisation of ORR peak currents with increase in the number of scan cycles for undoped and doped-CoPyPc-MWCNT, respectively (only scans 90-100 are shown).



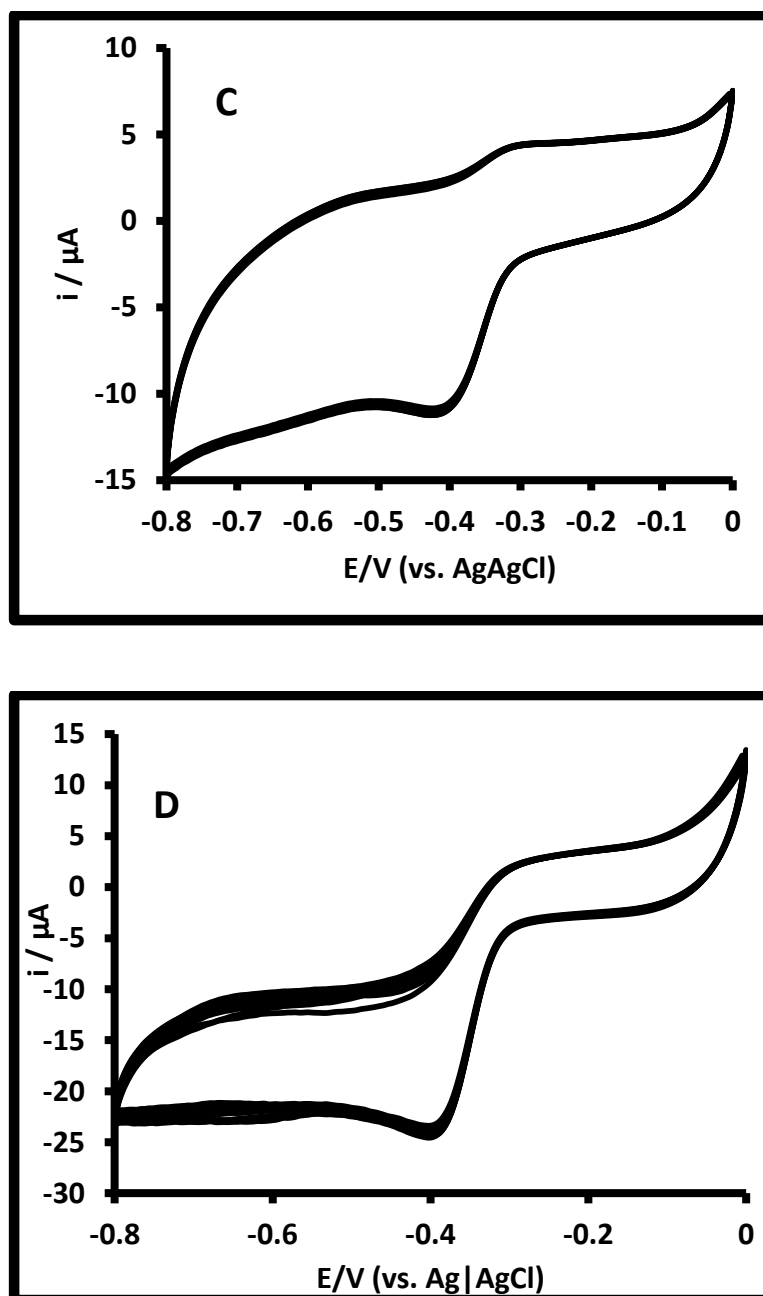


Fig. 5.28. CVs showing the effect of continuous cyclisation on ORR using iodine doped-CoPyPc-MWCNT (A) and undoped CoPyPc-MWCNT (B) nanocomposites in air saturated 0.5M NaOH. (C) and (D) shows current stabilization with increase in number of scans (only scans 90 to 100 are shown) for undoped and doped-CoPyPc-MWCNT, respectively. Scan rate = 100mV/s.

The average number of electrons involved in the ORR activity was determined by the RDE studies from the experimental data in Fig. 5.29. The data was analysed using the Koutecky-Levich equation (eqn 4.3).

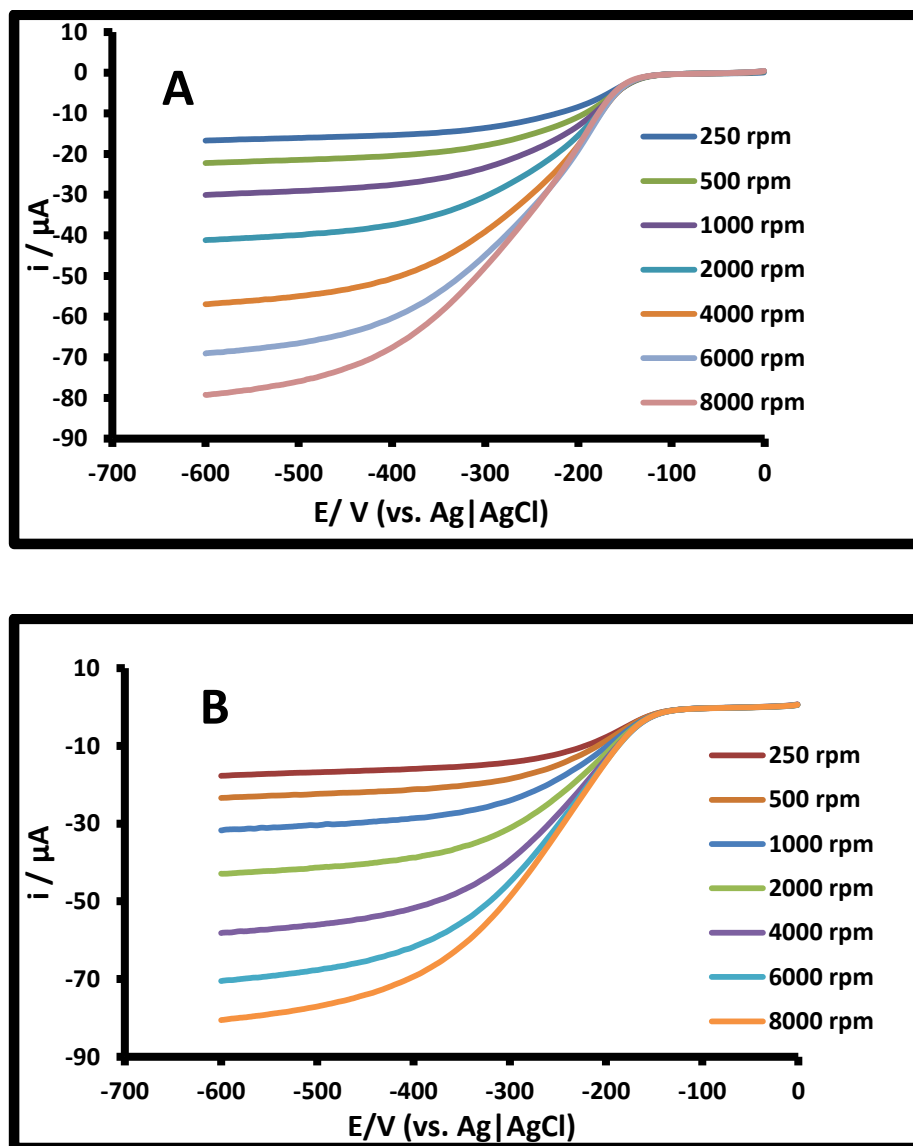


Fig. 5.29. Linear sweep voltammograms for ORR in air saturated 0.5 M NaOH on CoPyPc-MWCNT (A) and iodine doped-CoPyPc-MWCNT (B) modified rotating disk glassy carbon electrode at different rotating rates. Scan rate: 10 mV/s.

By comparing the catalytic limiting currents at the same potential and rotational speed e.g. 600 mV at 400 rpm, we observed that the catalytic current increased by 26% after doping. The number of electrons involved when using undoped CoPyPc-MWCNT and iodine doped CoPyPc-MWCNT nanocomposites were found to be 3.46 and 3.72, respectively. The values are close to 4 (more so for iodine doped CoPyPc-MWCNT) for direct four electron reduction of oxygen.

5.4. Methanol Crossover effects.

5.4.1. Chronoamperometry Studies.

Fig. 5.30 shows chronoamperometric responses under magnetic stirring and argon protection, followed by immediate introduction air at -0.45 V. The red arrows show the end of argon protection and introduction of air. The black arrows show the introduction of 3 M MeOH into the electrochemical cell. The currents for rGNS-2-CoPyPc were observed to be lower than rGNS-2-CdSe QDs-CoPyPc, implying that CdSe QDs play a significant role in the overall performance of the nanocomposite. The currents in the absence of reduced graphene (i.e. for CoPyPc alone) were generally lower than the nanocomposite. This further demonstrates the enhancement of performance of metallophthalocyanines supported on reduced graphenes towards ORR. Unlike in rGNS-2-CdSe QDs-CoPyPc, a decrease in current was observed with CoTAPc and CoPyPc on addition of MeOH, and the effect of presence of MeOH was more pronounced on the CoTAPc-GCE than CoPyPc-GCE. This stability can be attributed to extra conjugation on CoPyPc since it is the only difference between these two systems. The rate of change of chronoamperometry currents (Δi) on the rising part of chronoamperomograms until a current of 10 mA

against time (Δt) i.e. $(\Delta i/\Delta t)$ for CoTAPc, CoPyPc, rGNS-2-CoPyPc and rGNS-2-CdSe-QDs-CoPyPc were found to be 0.065 mA/s, 0.25 mA/s, 0.093 mA/s and 0.21 mA/s, respectively.

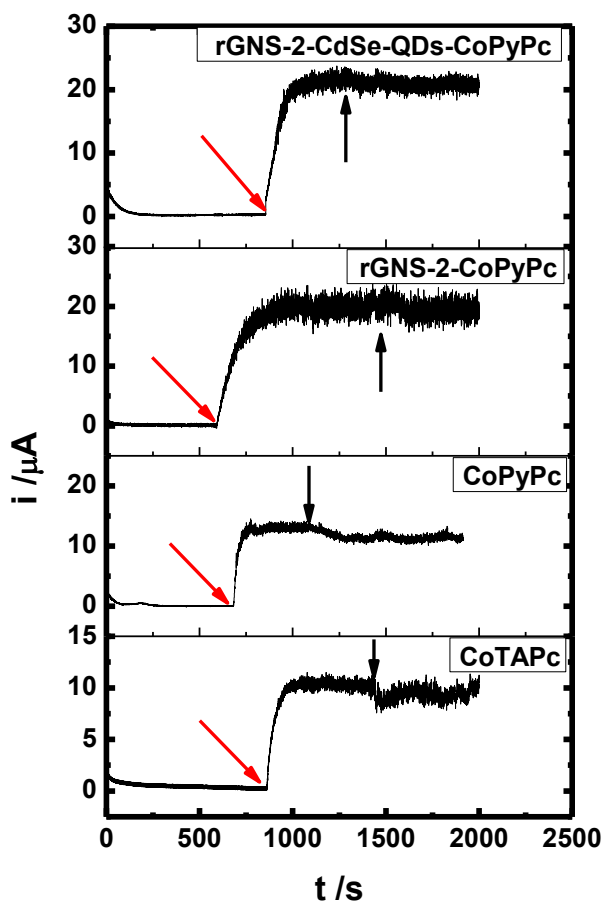


Fig. 5.30. Chronoamperometric responses obtained at the CoTAPc-GCE, CoPyPc-GCE, CoPyPc-rGNS-2-GCE, and CoPyPc-rGNS-2-CdSe-QDs-GCE in 0.5 M NaOH.

In this respect, CoPyPc and CoPyPc-rGNS-2-CdSe-QDs prove to have better electrocatalytic activity in relation to electron transfer and sensitivity. However, the maximum catalytic currents for CoPyPc are almost half of CoPyPc-rGNS-2-CdSe-QDs. Overall, this makes CoPyPc-rGNS-2-CdSe-QDs nanocomposite a competing platform for ORR activity in comparison to current Pt catalysts which suffer a lot

due to MeOH poisoning. It has been demonstrated that the ORR activity of platinum supported on carbon (Pt/C) on glassy carbon electrode is very sluggish with a sharp decrease in current upon addition of 3 M MeOH [107].

5.4.2. EIS.

The CoPyPc-rGNS-2-CdSe-QDs nanocomposite was further probed into the possible crossover effect on electron transfer since previous electrochemical characterizations have shown it to be the best in this study. The Randles equivalent circuit, $R_1(R_2Q_1)$, was used to estimate the resistance to charge transfer, where R_1 is solution resistance and R_2 is the resistance to charge transfer. The Bode plot (Fig. 5.31) shows that the phase angles are approximately the same (-69°), and shifted to the same frequency ($\log(f) \approx 0.4$).

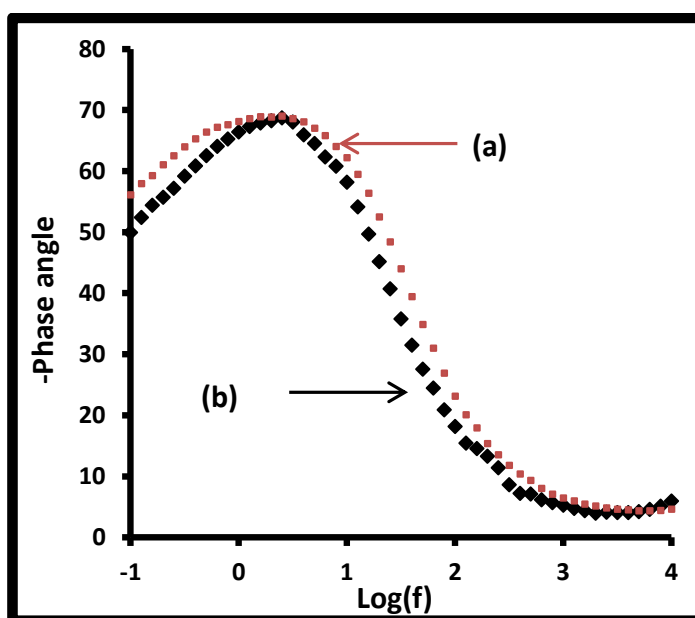


Fig. 5.31. Bode plots obtained using CoPyPc-rGNS-2-CdSe-QDs on GCE in air saturated 0.5 M NaOH in presence (a) and in the absence (b) of 3 M MeOH.

The EIS results for CoPyPc-rGNS-2-CdSe-QDs are summarized in Table 5.7. The same behaviour observed here under these two different conditions is a confirmation that rGNS-2-CdSe-QDs-CoPyPc nanocomposite has improved tolerance to methanol crossover.

Table 5.7. A summary of EIS data using CoPyPc-rGNS-2-CdSe-QDs nanocomposite.

EIS condition	Rct	n	-Phase angle	Log (f)
In the absence of MeOH	$50.4 \pm 3.54\%$	$0.79 \pm 0.88\%$	69°	≈ 0.4
In the presence of MeOH	$55.5 \pm 5.45\%$	$0.82 \pm 0.82\%$	69°	≈ 0.4

5.5. Conclusion

This chapter has shown that mixed nanocomposites of CoPyPc-MWCNTs and CoTAPc-MWCNTs have approximately the same E_p (≈ 0.6 V) for l-cysteine oxidation. Polymerised nanocomposites have better l-cysteine oxidation potentials (less positive) and lower LODs relative to nanocomposites involving monomeric MPcs. The CoPyPc-MWCNT (linked) nanocomposite performs better than the mixed nanocomposite in terms of l-cysteine oxidation, displaying less positive oxidation potentials and lower LODs. Hence, covalently linked and polymerised nanomposites have the suitability for preparation of electrocatalyst. Furthermore, iodine doping plays a significant role in improving onset potentials for ORR.

Chapter Six: Conclusions.

6. Conclusions.

Comparative electrocatalytic behaviour of the modified GCE surfaces was performed. Adding carbon nanomaterials first (MWCNTs and rGNS), followed by drop-dry of the MPc on top of the MWCNTs or rGNS on GCE proved to have better electrocatalytic behaviour towards L-cysteine, PQ and ORR catalysis than other premixed surfaces. These surfaces gave better LOD, low response time and better sensitivity, lower R_{ct} , and higher kinetic rate constant values in relation to other surfaces under study. CV, CA, SECM and EIS data agree well with each other thereby giving these results greater validity for practical applications. Because of such enhanced electrocatalytic properties, addition of a metallo-phthalocyanine on top of the carbon nanomaterials during the fabrication of sensors is hereby encouraged to produce nanostructured electrode surfaces with high performance.

The reduction of GONS for the preparation of CoTAPc-rGNS-2-MWCNT nanocomposite was successful. The prepared nanocomposite was intensively characterized to demonstrate the influence of MWCNT and of the reduced graphene nanosheets on the electrocatalytic activity of CoTAPc. The activity of CoTAPc-rGNS-2-MWCNT towards the test analyte (paraquat) has demonstrated to be more superior to individual components (rGNS-2-GCE, rGNS-2-MWCNT-GCE, CoTAPc or CoTAPc-MWCNT). It has also been demonstrated that the prepared nanocomposite for PQ sensing and quantification has a strong resistance to fouling. As a result such architecture can have wide applications in routine monitoring of pesticides levels in water bodies for human safety.

Cobalt metallophthalocyanine derivatives were electropolymerised on both the bare GCE and MWCNT-GCE to form polymerised electrocatalytic thin films. From the

evaluation of the electrocatalytic performance of the polymer films, it has been found out that polymer films behaved better when supported on MWCNT than on bare GCE. Improved sensitivity, kinetic rate constants and lower LODs were obtained for these nanocomposites. The polymer of the new CoPyPc competes well with the known CoTAPc. Furthermore, it involves less stages of preparation than CoTAPc, hence less time and better yields, making it suitable for the development of very cheap and affordable electrocatalytic platforms for sensing some physiological thiols and related applications.

Electrochemical characterization has demonstrated that the nanocomposite fabricated by covalently linking the metallophthalocyanine to MWCNT performs well than the mixed nanocomposite. Electrocatalytic activities of individual components of the nanocomposites have shown to be rather sluggish. The linked nanocomposite has shown resistance to surface fouling by oxidation products of the test analyte (l-cysteine), as well as low LOD. Again, the nanocomposite from the new CoPyPc can be used to detect thiols in aqueous environments, and can allow for applications in diagnosis of thiols-related diseases in human beings.

The inclusion of CdSe-QDs in-between graphene nanosheets was successful in improving the ORR potential for the graphene. This was further enhanced by decoration of the rGNS-2-CdSe-QDs nanocomposite with a CoPyPc. CoPyPc-rGNS-2-CdSe-QDs nanocomposite has better ORR electrocatalytic activity than the bare GCE and individual components. However, CoPyPc-rGNS-2 is also promising. CoPyPc-rGNS-2-CdSe-QDs showed remarkably high tolerance to methanol crossover effect. CoPyPc-rGNS-2-CdSe-QDs properties makes this nanocomposite a suitable candidate

to be exploited for development of non-precious metal fuel cells which are cheaper than Pt-based, as well as promoting use of non-polluting energy sources.

Iodine doping of CoPyPc resulted in the red-shifting of the Q band. The doped CoPyPc showed enhanced electrocatalytic behaviour towards oxygen reduction reaction when supported on MWCNT. The iodine doped non-precious MPc shows good electrocatalytic activity towards ORR, making it a potential candidate to compete well with the current precious Pt electrocatalysts in fuel cell application or oxygen sensing in general.

In summary, the exceptional catalytic activity of the easy-to-prepare nanocomposites is ascribed to their excellent conductivity, high electrocatalytically accessible surface area, good stability and the synergistic effects of the individual components within the nanocomposites. Thus, these architectures fabricated in this work could be viewed as good candidates for both sensor and fuel cell development for everyday use.

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