# TABLE OF CONTENTS

ABSTRACT......................................................................................................................... i  
ACKNOWLEDGEMENT........................................................................................................ ii  
LIST OF FIGURES............................................................................................................... vii  
LIST OF TABLES................................................................................................................ xiii  
LIST OF SCHEMES............................................................................................................ xiv  
LIST OF TERMS AND ABBREVIATIONS............................................................................. xvi  

1 Introduction 1  
1.1 Chemically Modified Electrodes.................................................................................. 1  
1.2 Carbon Nanomaterials ................................................................................................ 3  
1.2.1 Graphene Oxide...................................................................................................... 3  
1.2.2 Graphite Nanopowder............................................................................................ 5  
1.2.3 Carbon Nanotubes................................................................................................ 5  
1.3 Polymers for Tailoring Electroactive Materials............................................................ 9  
1.3.1 Chitosan.................................................................................................................. 9  
1.3.2 Poly Ionic liquids.................................................................................................... 9  
1.3.3 Nafion.................................................................................................................... 10  
1.4 CNT Based CMEs...................................................................................................... 11  
1.4.1 CNT-Metal Bipyridyl Complexes.......................................................................... 12  
1.4.2 CNT-Quinone Hybrids.......................................................................................... 13  
1.5 Objectives and Scope of the Present Work................................................................. 14  

2 Electrochemical Platform for the Detection of Lymphatic Filarial Parasite- Wuchereria bancrofti in Vector Samples Using Graphene-Oxide Chitosan Chemically Modified Electrode with Ru(bpy)$_3^{2+}$ Redox Probe 17  
2.1 Introduction................................................................................................................. 17  
2.2 Experimental Section.................................................................................................. 20  
2.2.1 Materials............................................................................................................... 20  
2.2.2 Instrumentation...................................................................................................... 21  
2.2.3 Fabrication of GCE/GO+Chit @P-DNA and Hybridization Reaction................. 22
2.2.4 Electrochemical Measurements

2.3 Results and Discussion

2.3.1 Physico-Chemical Characterization of GO+Chit nanocomposite

2.3.2 Electrochemical Characterization of GO+Chit modified GC electrode

2.3.3 Electrochemical Behaviours of Different DNA Modified GCE/GO+Chit Electrodes

2.4 Conclusion

3 In-situ Ion-Exchanging of Ferricyanide on Aromatic Unit Bearing Poly Ionic Liquid – Graphite Nanopowder (PIL-GNP) Composite Chemically Modified Electrode and its Selective Electrocatalytic Oxidation and Sensing of Ascorbic Acid

3.1 Introduction

3.2 Experimental Section

3.2.1 Materials and Reagents

3.2.2 Instrumentation

3.2.3 Procedure for GCE/GNP-PIL@Fe(CN)$_6^{3-}$ Preparation

3.3 Results and Discussion

3.3.1 Electrochemical Behavior of GCE/GNP-PIL@Fe(CN)$_6^{3-}$

3.3.2 Physicochemical Characterization of GCE/GNP-PIL@Fe(CN)$_6^{3-}$

3.3.3 Electrocatalytic Behavior of GCE/GNP-PIL@Fe(CN)$_6^{3-}$

3.4 Conclusion

4 In-situ Complexation of Copper Ion as Copper-Aqua-2,2-Bipyridyl Complex on Bipyridyl Adsorbed MWCNT Modified Electrode Prepared by New Strategy for Elegant Electrocatalytic Reduction and Sensing of Hydrogen Peroxide

4.1 Introduction

4.2 Experimental Section

4.2.1 Chemicals and Materials

4.2.2 Instrumentation

4.2.3 Preparation of Chemically Modified Electrode

4.2.4 Real Sample Preparation

4.3 Results and Discussion

4.3.1 Electrochemical Behavior of GCE/Nf-MWCNT@bpy-Cu$^{2+}$
4.3.2 Physicochemical Characterization of GCE/MWCNT@bpy-Cu$^{2+}$ | 62
4.3.3 Electrocatalysis of GCE/Nf-MWCNT@bpy-Cu$^{2+}$ Towards H$_2$O$_2$ | 65

4.4 Conclusion | 74

5  
**In-situ** derivatization of an intrinsic iron impurity as a surface-confined iron(II)tris(2,2'-bipyridine) complex on MWCNT and its application for selective electrochemical sensing of DNA’s purine bases | 76

5.1 Introduction | 76
5.2 Experimental Section | 78
5.2.1 Materials and Reagents | 78
5.2.2 Instrumentation | 79
5.2.3 Procedure for GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ Preparation | 79

5.3 Results and Discussion | 80
5.3.1 Electrochemical Behavior of GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ | 80
5.3.2 Physicochemical Characterization of GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ | 83
5.3.3 Electroanalytical application of GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ | 85

5.4 Conclusion | 88

6  
**In-situ** Electrochemical Transformation of Aminobenzene Sulfonic Acid Isomers to Respective Surface-Confined Redox Active Quinones by Passing Polyaniline on MWCNT Surface for NADH Sensing | 90

6.1 Introduction | 90
6.2 Experimental Section | 92
6.2.1 Materials and Reagents | 92
6.2.2 Instrumentation | 92
6.2.3 Procedure | 94

6.3 Results and Discussion | 94
6.3.1 Electrochemical Oxidation of SA on GCE/MWCNT Modified Electrode | 94
6.3.2 Physico-chemical characterization of GCE/MWCNT@SA-Oxid | 96
6.3.3 Electrocatalysis of GCE/MWCNT@HQ towards NADH | 102

6.4 Conclusion | 104
7  In-situ Electrochemical Oxidation of Indole and Trapping of an Redox Active Tetraone as Surface Confined Intermediate on MWCNT Modified Electrode and its Electrocatalytic Oxidation/Reduction of Hydrazine and H₂O₂ in Physiological Solution

7.1 Introduction .............................................................................................. 105
7.2 Experimental Section ............................................................................. 107
  7.2.1 Chemicals and Materials ................................................................. 107
  7.2.2 Instrumentation .............................................................................. 108
  7.2.3 Preparation of the Indole Based Chemically Modified Electrode........ 108
7.3 Results and Discussion .......................................................................... 109
  7.3.1 Electrochemical Oxidation of Indole as Selective Quinone .......... 109
  7.3.2 Physicochemical Characterization of MWCNT@Ind-Oxid .......... 113
  7.3.3 Electroanalytical application of GEC/MWCNT@Ind-Tetraone ...... 119
7.4 Conclusion ............................................................................................... 123

8  Summary and Conclusions ....................................................................... 124

9  List of Publications .................................................................................... 125

10 References ............................................................................................... 126
LIST OF FIGURES

2.1 Comparative Responses of (A) Transmission Electron Microscopy (B) Raman Spectroscopy and (C) FTIR/KBr of (a) SPCE/GO and (b) SPCE/GO+Chit Modified Electrodes.......................... 25

2.2 Comparison of GCE/GO (curve a; black) and GCE/GO-Chit (curve b; pink) by (A) CV and (B) EIS Measurements Using 5 mM K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ in 0.1 M KCl. Inset: Randles Equivalent Circuit.......................... 26

2.3 (A) CV, (B) DPV and (C) EIS Measurements of GCE/GO+Chit (Curve a; black), GCE/GO+Chit@P-DNA (Curve b; blue), GCE/GO+Chit@P-T DNA (Curve c; red) and GCE/GO+Chit@P-Mis DNA (Curve d; green) Using 5 mM Ru(bpy)$_3^{2+}$ in 0.1 M KCl.......................... 29

2.4 Impedimetric Response of Different Concentrations ($10^{-13}$ To $10^6$) of Probe DNA (P-DNA) on GCE/GO+Chit Electrode. Error Bars Calculated with Standard Deviation Corresponding to Triplicative Experiments......................... 30

2.5 (A) ESI Responses of GCE/GO+Chit@P-DNA (curve a), and its Hybridization with PCR Ampicons of Wucherria bancrofti (GCE/GO+Chit@P-T$_{WB}$ DNA; curve b) and Brugia malayi (GCE/GO+Chit@P-Mis$_{BM}$ ; curve c) DNA in 5 mM Ru(bpy)$_3^{2+}$ in 0.1 M KCl. (B) ESI Responses of GCE/GO+Chit@P-DNA after Hybridization with Different Concentration Target Ssp I Repeat of Wucherria bancrofti ssDNA (from a to f, the Concentrations are 0.004, 0.006, 0.008, 0.016, 0.5 and 1µg) and (C) Calibration Plot...................................................... 31

2.6 The Comparison of Impedimetric Response of Probe DNA Alone Before Hybridization and After Hybridization with Complementary and Non-Complementary. Error Bars Calculated with Standard Deviation Corresponding for Six Replicative Experiments.......................................... 32

3.1 Twenty Continuous CV Responses of (A) GCE@PIL and (B) GCE/GNP-PIL in 2 mM K$_3$Fe(CN)$_6^{3-}$ Solution (Curve a) and Their stability (Curve b) in pH 7 PBS. (C) Effect of Scan rate (10-500 mV s$^{-1}$) on the CV Response of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ in pH 7 PBS. Plots of (D) log $i_p$ vs log$v$, (E) $E_p$ vs log$v$ and (F) Effect of pH Solutions on the CV Response of GCE/GNP-PIL@Fe(CN)$_6^{3-}$ at a scanrate 50 mV s$^{-1}$ ........................................ 40

3.2 (A-F) CV Response of Ferricyanide Surface Confined Various Carbon Nanomaterials - PIL Modified Electrodes in pH 7 PBS at a $v$ = 50 mV s$^{-1}$. Insets are its $\Delta E$ and $\Gamma_{FeCN}$ Values. ......................................................... 42
3.3 (A-F) CV Responses of Ferricyanide Confined Various Poly Ionic Liquids/GNP Modified Electrodes in pH 7 PBS at a \( v = 50 \) mV s\(^{-1}\) …………

3.4 SEM Images of (A-B) SPCE/GNP, (C-D) SPCE/GNP-PIL and (E-F) SPCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) at Different Magnifications………………

3.5 Comparative (A) Raman and (B) FT-IR patterns of GNP (curve a) and GNP-PIL (curve b) and GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) (curve c) Samples……

3.6 (A) CV of GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) without (curve a) and with 1mM AA (curve b) Respectively in 0.1 M PBS at a \( v = 10 \) mV s\(^{-1}\). Curve c is the Response of GCE/GNP with 1mM AA. (B) Effect of Scan rate on CV Response of GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) Electrode in Presence of 2 mM Ascorbic Acid in pH 7 PBS. Plots of (C) \( i_{pa} vs v^{1/2} \), (D) \( i_{pa}/v^{1/2} vs v \) and (E) \( E_{pa} vs \log v \). (F) Comparative Bar Diagram Depicting Electrocatalytic AA (1 mM) Oxidation Current, Against Various Carbons – PIL Modified Electrodes Ion-Exchanged with Ferricyanide in pH 7 PBS………………

3.7 Comparative Amperometric I-T Responses of (A) GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) (curve a), GCE/GNP-PIL (curve b) and GCE/GNP (curve c) for Detection of 25 \( \mu \)M AA with Calibration Plot of GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) as Inset; (B) Interference Study of GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) Towards AA with Coexisting Biochemicals; (C and D) Real Sample Analysis of AA in Commercial Juice Samples Using GCE/GNP-PIL@Fe(CN)\(_6\)\(^{3-}\) by Standard Addition Approach at \( E_{app} = 0.15 \) V vs Ag/AgCl in pH 7 PBS…………………………………………………

4.1 CV Responses of (A) GCE@Cu\(^{+}\), (B) GCE/MWCNT@Cu\(^{n+}\), (C) GCE@bpy-Cu\(^{2+}\), (D) GCE/MWCNT@bpy-Cu\(^{2+}\) and (E) GCE/Nf-MWCNT@bpy-Cu\(^{2+}\) at a \( v = 50 \) mVs\(^{-1}\) in pH-7 PBS. (F) Peak current (\( i_{pa} \)) vs Different carbon matrices. Fig. 1D, Curve b is CV Response of GCE/MWCNT@bpy-Cu\(^{2+}\) in pH-7 PBS Prepared by Immersion Method in 2 mM CuSO\(_4\) at \( v = 50 \) mVs\(^{-1}\)…………………………

4.2 Effect of Scan rate in pH 7 PBS (A) and Solution pH at \( v = 50 \) mV s\(^{-1}\) (B) on CV Response of GCE/Nf-MWCNT@bpy-Cu\(^{2+}\). Insets are Plots of (a) \( \log i_{p} vs \log v \), (b) \( E_{p} vs \log v \) and (c) \( E_{pc} vs pH \) …………………

4.3 Typical SEM Images of (A) ITO/CNT, (B) ITO/MWCNT@bpy and (C) ITO/MWCNT@bpy-Cu\(^{2+}\) at Different Magnifications………………

4.4 (A) Raman Spectra of Au-SPE/MWCNT (curve a), Au-SPE/MWCNT@bpy (curve b) and Au-SPE/MWCNT@bpy-Cu\(^{2+}\) (curve c); (B) FTIR/KBr Responses of MWCNT (curve a), bpy (curve b) and MWCNT@bpy-Cu\(^{2+}\) (curve c) and (C) Electrospray Ionisation Mass Spectrometry (ESI-MS) of Ethanolic Extract of GCE/MWCNT@bpy-Cu\(^{2+}\)…………………………

4.5 (A) CV Response of GCE/Nf-MWCNT@bpy-Cu\(^{2+}\) without (curve a) and
with 500 µM of H₂O₂ (curve b), GCE@bpy-Cu²⁺ (curve c) and GCE/Nf-MWCNT@Cu⁸⁺ (curve d) with 500 µM of H₂O₂ in pH 7 PBS at v = 10 mV s⁻¹; (B) CVs of GCE/Nf-MWCNT@bpy-Cu²⁺ Electrode in Presence of 1.5 mM H₂O₂ in pH 7 PBS at v = 5, 10, 20, 30, 50, 70, 100, 150, 200, 400, 500 mV s⁻¹ and Insets are Plots of (a) iₚc vs v½, (b) iₚc/v½ vs v, (c) Eₚc vs logv; (C) CV responses of GCE/Nf-MWCNT@bpy-Cu²⁺ Towards Successive Additions of H₂O₂ solution at v = 10 mV s⁻¹ and Inset is a plot of (d) logiₚc vs [H₂O₂] and (D) CV Response of GCE/Nf-MWCNT@bpy-Cu²⁺ without (curve a) and with 500 µM of H₂O₂ (curve b) in pH 7 PBS at v = 5 mV s⁻¹ and Inset is a (e) Tafel plot

4.6 RDE Responses for the Reduction of 500 µM H₂O₂ on GCE/Nf-MWCNT@bpy-Cu²⁺ at Different RPMs (50-500 RPM) at v = 10 mV s⁻¹; (B) Levich and (C) Koutecky Levich Plots at Different Potentials (E₁-E₈: -0.25, -0.3, -0.35, -0.4, -0.45, -0.5, -0.55 and -0.6 V vs Ag/AgCl) for the RDE Response

4.7 (A) Comparative Amperometric I-T Responses of (A) GCE/Nf-MWCNT@bpy-Cu²⁺ (curve a), GCE/Nf-MWCNT (curve b) and GCE/Nf-MWCNT@bpy (curve c) with 50 µM H₂O₂ Continuous Spikes and (B) Interference Study of GCE/Nf-MWCNT@bpy-Cu²⁺ Towards H₂O₂ with Co-existing Biochemicals of 100 µM Concentration Each at E_app = -0.2 V vs Ag/AgCl

4.8 (A) FIA Response of the GCE/Nf-MWCNT@bpy-Cu²⁺ With Increasing Concentration of H₂O₂ at E_app = -0.2 V vs Ag/AgCl and Hₓ = 700 µL min⁻¹ using 0.1 M PBS (pH 7) as a Carrier Buffer Solution and Inset is a Calibration Plot. (B) Reproducibility of GCE/Nf-MWCNT@bpy-Cu²⁺ with 1 µM H₂O₂. (C) FIA Response of GCE/Nf-MWCNT@bpy-Cu²⁺ Towards Various Electro-active Biochemicals of 100 µM Concentration of Each

4.9 FIA Responses of GCE/Nf-MWCNT@bpy-Cu²⁺ for Real Samples (A and B) Studies of H₂O₂ by Standard Addition Approach at E_app = -0.2 V vs Ag/AgCl and Hₓ = 700 µL min⁻¹ in 0.1 M PBS as Carrier Solution with Inset Calibration Plots

5.1 CV Responses of Bpy Ligand Adsorbed (A) GCE/Nf-MWCNT-*Fe (a) and Control Experiments Such as Bpy Adsorbed GCE/MWCNT-*Fe (without Nafion; Curve b) and GCE/Nf-MWCNT-*Fe (without Bpy; Curve c) in pH 7 PBS; (B) CV Response of (a) a Chemically Simulated GCE/MWCNT+Nf+Fe(bpy)₃²⁺ Sim Electrode (Prepared by Coating of Nafion+Fe(bpy)₃²⁺ Mixture on GCE/MWCNT-*Fe; Sim = simulated) and (b) GCE/MWCNT-*Fe; (C) Continuous CV Responses of GCE/Nf-Fe(bpy)₃²⁺ in pH 2 (a) and its Stability in pH-7 PBS (b) at Scan rate 50 mV s⁻¹ and (D) Plot of Relative % of Anodic Peak Current (i_pa) vs Number of Potential Cycles of the Optimal (GCE/Nf-MWCNT-*Fe(bpy)₃²⁺) and
GCE/Nf-Fe(bpy)$_3^{2+}$ (Ion Exchange) Systems. ..............................................

5.2 CVs of GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ in pH 7 PBS at Different Scan rates and its Typical $i_{pa}$ and $i_{pc}$ vs Scan rate Plot (inset)................................. 81

5.3 CV Responses of Bpy Ligand Adsorbed Different Carbons and Iron Oxide; (A) GCE/Nf-f-MWCNT-*Fe, (B) GCE/Nf-p-MWCNT-*Fe, (C) GCE/Nf-GNP and (D) GCE/Nf-Fe$_3$O$_4$/Fe$_2$O$_3$. Note: f-MWCNT = Functionalised MWCNT; p-MWCNT = Purified MWCNT; GNP = Graphite Nanopowder. 82

5.4 (A) Raman spectroscopy, (B) FT-IR/KBr and (C) UV-Vis (as Ethanoic Extracts) Responses of Bpy Adsorbed GCE/Nf-MWCNT-*Fe and its Control Samples................................................................. 83

5.5 (A) Typical Liquid Chromatographic Pattern and (B) Electron Spray Ionisation Coupled Mass Spectrum Response of an Ethanoic Extract GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ at 5.85 min Retention Time in the LC Response.............................................................. 84

5.6 (A) and (D) are CV Responses of GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ without (Curve a) and with 1 mM (Curve b) of Adenine (A) and Guanine (G) and Unmodified GCE/Nf-MWCNT-*Fe with 1 mM of Adenine and Guanine (Curve c) Respectively; (B and E) FIA Responses of GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ with Increasing Concentration of Adenine (E$_{app}$$_{A+G}$ = 1.0V) and Guanine (E$_{app}$$_G$ = 0.7V) with pH 7 PBS Carrier Solution and its Calibration Plots as Insets; (C and F) FIA-Interference Study with GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$ at E$_{app}$ = 1.0 V and 0.7 V vs Ag/AgCl. Inset Figures: Curve a, b and c are Twelve Repeated FIA of Adenine and Guanine on GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$, GCE/Nf-Fe(bpy)$_3^{2+}$ and GCE/Nf-MWCNT-*Fe Respectively. Note: Optimal=GCE/Nf-MWCNT-*Fe(bpy)$_3^{2+}$; T = Thymine; C = Cytosine. [H$_f$ = 0.9 ml.min$^{-1}$]......................................................... 88

6.1 (A) Twenty Continuous CV Responses of GCE (curve a), GCE/MWCNT (curve b and C) with 15 mM p-Aminobenzene Sulfonic Acid (p-SA) at Different Potential Windows (Set-I and Set-II), (B) GCE/MWCNT@SA-Oxid at a Scan rate 50 mV s$^{-1}$ in 0.1 M pH 7 PBS and (C) Plot of Anodic Peak Current vs Carbon Matrix for the Formation of Carbon@SA-Oxid system........................................................................................................ 95

6.2 (A) Effect of Scan rate (5-400 mVs$^{-1}$) on the CV of GCE/MWCNT@SA-Oxid in pH 7 PBS and (B) Plot of log $i_{pa}$ vs logv. (C) Effect of Solution pH (4−11) on the CV Response of GCE/MWCNT@SA-Oxid at a Fixed Scan rate of 50 mV s$^{-1}$ and (D) Plot of E$_{pa}$ vs pH. [Note: GCE/MWCNT@SA-Oxid = GCE/MWCNT@HQ].................................................................................................................. 96

6.3 Comparative Raman (A), XRD (B) and FTIR (C) Response of Various Systems......................................................................................................................... 97
6.4 TEM Images of (a) MWCNT@poly-SA, (b) MWCNT@HQ, (c) MWCNT with Insets of Cartoons of Respective Systems

6.5 (A) In situ-EQCM-Au/MWCNT Response with 15mM p-SA in pH 7 PBS at \( v = 50 \text{ mV s}^{-1} \); Plots of (B) \( \Delta n \) vs E and (C and D) \( \Delta n \) vs Q of 3 and 4\(^{th}\) cycles. Inset of A is the Photograph of EQCM-Au/MWCNT and C and D are Respective Organic Compounds Involved in the Reaction Steps

6.6 GC-Mass Spectra of a Methanolic Extract of GCE/MWCNT@SA-Oxid

6.7 Continuous CV Response of (A) Naked Catechol (curve a), Ortho-SA (curve b); (B) Naked Resorcinol (curve a) and Meta-SA (curve b) on GCE/MWCNT and (C) GCE/MWCNT@SA-Oxid Formation without (curve a) and with 100µM H\(_2\)O\(_2\) in N\(_2\)-purged pH 7 PBS at a Scan rate 50 mV s\(^{-1}\). [SA-Oxid = HQ]

6.8 CV Responses of Various SA Isomers Modified GCE/MWCNT Electrodes Prepared at Different Electrolyte Condition, in pH-7 0.1M PBS at a Scan rate 50 mV s\(^{-1}\)

6.9 (A) Comparative CV Responses of GCE/MWCNT@HQ without (curve a) and with 1 mM of NADH (curve b) and GCE/MWCNT with 1 mM NADH (curve c) in pH 7 PBS at \( v = 50 \text{ mV s}^{-1} \); (B & C) Amperometric I-T Responses of GCE/MWCNT@HQ (curve a) and GCE/MWCNT (curve b) with Continuous Spikes of 50 \( \mu \text{M} \) of NADH (B) or Other Interfering Chemicals (C) at an Applied Potential (E\(_{\text{app}}\)) of 150 mV vs Ag/AgCl in pH 7 PBS

7.1 CV Responses of Indole Adsorbed (A) GCE (GCE@Ind-Oxid; Curve a) and GCE/MWCNT (GCE/MWCNT@Ind-Oxid; Curve b), (B) pyrrole (GCE/MWCNT@Pyr), (C) 2 Me-Indole (GCE/MWCNT@2-Me Ind), (D) 3-Carbaxaldehyde Indole (GCE/MWCNT@3-CHO Ind), (E) Isatin (GCE/MWCNT@Isatin) and (F) Indene (GCE/MWCNT@Indene) Adsorbed on GCE/MWCNT in pH 7 PBS at a \( v = 50 \text{ mV s}^{-1} \); Note: Ind-Oxid = Ind-Tetraone

7.2 (A) Effect of Scan rate (10-300 mV s\(^{-1}\)) on the CV Response of GCE/MWCNT@Ind-Oxid in pH 7 PBS. Plots of (B) \( i_p \) vs v, (C and D) log\( i_p \) vs logv. (E) Effect of Solution pH on the CV Response of GCE/MWCNT@Ind-Oxid at a \( v = 50 \text{ mV s}^{-1} \)and (F) Plot of E\(_p\) vs pH; Note: Ind-Oxid = Ind-Tetraone

7.3 Effect of Potential Scan Direction on CV Response of GCE/MWCNT@Ind-Oxid in pH 7 PBS at \( v = 50 \text{ mV s}^{-1} \). (A) E-cycling Experiments with a Fixed Starting Potential of \( -0.6 \text{ V} \) and Varying End Potentials of (a.) 0.1, (b.) 0.4, (c.) 0.5 and (d.) 0.6 V Versus Ag/AgCl. (B) E-cycling Experiments with a Fixed End Potential of 0.4 V and Varying Starting Potentials of (e.) \(-0.6, (f.) -0.5, (g.) -0.4 \text{ and (h.) } -0.3 \text{ V Versus Ag/AgCl; Note: Ind-Oxid = Ind-}
7.4 TEM Images of (A and B) MWCNT (Unmodified) and (C and D) MWCNT@Ind-Oxid at Different Magnifications; Note: Ind-Oxid = Ind-Tetraone

7.5 Comparative (A) Raman Spectroscopic Response of (a) SPCE/MWCNT, (b) SPCE/MWCNT@Ind$_{ads}$ and SPCE/MWCNT@Ind-Oxid and (B) FTIR/KBr Responses of (a) SPCE/MWCNT, (b) Indole and (c) SPCE/MWCNT@Ind-Oxid (Note: SPCE = Screen-Printed Carbon Electrode, Ind-Oxid = Ind-Tetraone)

7.6 C 1s and O 1s XPS Spectrum of (a) SPCE/MWCNT, (b) SPCE/MWCNT@Ind$_{ads}$ and SPCE/MWCNT@Ind-Oxid. Note: SPCE = Screen-Printed Carbon Electrode, Ind-Oxid = Ind-Tetraone

7.7 GC-Mass Responses of Ethanolic Extracts of (A and B) MWCNT@Ind-Oxid and (C) MWCNT@Ind$_{ads}$ at Retention Times 14.25, 16.04 min and 10.32 Showing the Presence of Indole Oxidised Products (1H indole-2,3dione or Isatin $m/z = 147.1$; 1H indole-2,3,4,7 Tetraone $m/z = 179.1$) and Indole ($m/z = 117.04$); Note: Ind-Oxid = Ind-Tetraone

7.8 Effect of Carbons on the Modified Electrode Preparation; CV Responses of (A) GCE/MWCNT@Ind-Tetraone, (B) GCE/p-MWCNT@Ind-Tetraone, (C) GCE/f-MWCNT@Ind-Tetraone, (D) GCE/SWCNT@Ind-Tetraone, (E) GCE/GNP@Ind-Tetraone and (F) GCE/AC@Ind-Tetraone in pH 7 PBS at a $v = 50$ mV s$^{-1}$

7.9 GCE/MWCNT@Ind-Tetraone Formation without (curve a) and with 100µM H$_2$O$_2$ (curve b) in N$_2$-Purged pH 7 PBS at a Scan rate 50 mV s$^{-1}$

7.10 (A) and (D) CV Responses of GCE/MWCNT@Ind-Tetraone without (curve a) and with 1 mM (curve b) Hydrazine and H$_2$O$_2$ and Unmodified GCE/MWCNT with 1 mM Hydrazine and H$_2$O$_2$ (curve c), Respectively; (B) and (E) CV Responses of GCE/MWCNT@Ind-Tetraone Towards Successive Additions of Hydrazine and H$_2$O$_2$ at $v = 10$ mV s$^{-1}$ Respectively; (C) and (F) Calibration Plots of Catalytic Currents ($i_p$) Versus [Hyd] and [H$_2$O$_2$] Respectively

7.11 (A) FIA Responses of GCE/MWCNT@Ind-Tetraone Towards Simultaneous Detection of a Mixture of Increasing Concentrations of Hydrazine (E$_{app}$= 0.35 V) and H$_2$O$_2$ (E$_{app}$= -0.15 V) with a pH 7 PBS Carrier Solution and Its Calibration Plots as Insets (a and b) Respectively. (B) FIA-interference Study on GCE/MWCNT@Ind-Tetraone at E$_{app}$= 0.35 and -0.15 V vs Ag/AgCl
## LIST OF TABLES

2.1 Oligonucleotide Sequences (ss-DNA) Employed for DNA Hybridization…… 21

2.2 PCR Amplicons Employed for DNA Hybridization in Real Sample Analysis. 21

2.3 Reproducibility of Synthetic Short Stranded Oligonucleotides……………… 29

2.4 Reproducibility of PCR Amplicons in Real Sample Analysis……………… 32

3.1 FE-SEM EDAX data of GCE/GNP@PIL-Fe(CN)$_6^{3-}$................................. 45

3.2 Comparison of the Analytical Performance of GCE/GNP@PIL-Fe(CN)$_6^{3-}$ for the Electrochemical Determination of Ascorbic Acid by Various Chemically Modified Electrodes…………………………………………………………… 51

3.3 Results of the Ascorbic Acid (AA) Real Sample Analysis Obtained with GCE/GNP@PIL-Fe(CN)$_6^{3-}$ by Amperometric $I$--$T$ Method at an Applied Potential of 0.15 V vs Ag/AgCl in pH ……………………………………….. 51

4.1 FE-SEM EDAX Data of GCE/MWCNT@bpy-Cu$^{2+}$................................. 63

4.2 Comparison of Electrochemical Performance Of GCE/Nf-MWCNT@bpy-Cu$^{2+}$ Towards H$_2$O$_2$ With Other Copper and HRP Based Chemically Modified Electrodes………………………………………………………………………………….. 73

4.3 Results of the H$_2$O$_2$ Real Sample Analysis Obtained Using a GCE/Nf-MWCNT@bpy-Cu$^{2+}$ by Flow Injection Analysis (FIA) at an $E_{app} = -0.2$ V vs Ag/AgCl in pH 7 PBS………………………………………… 74

6.1 Comparison of the Analytical Performance of GCE/MWCNT@HQ for the Electrochemical Determination of NADH by Various Quinone Based Chemically Modified Electrodes 103

7.1 Comparison of the Analytical Performance of GCE/MWCNT@Ind-Tetraone for the Electrochemical Determination of Hydrazine and H$_2$O$_2$ by Various Quinone Tethered MWCNT Modified Electrodes. 122

7.2 Real Sample Analysis of Hydrazine and H$_2$O$_2$ in Water Samples by Using the FIA-GCE/MWCNT@Ind-Tetraone System………………… 123
LIST OF SCHEMES

1.1 Schematic Representation for the Oxidation Reaction of A→B on Bare (A) and Mediated Conditions (B). The Terms P and Q Correspond to the Reversible Mediator of Reduced and Oxidized States, Respectively. The $E_{\text{obs}}$, $E^\circ_{\text{p/Q}}$, $E^\circ_{\text{a/B}}$ and $\eta$ Correspond to Uncatalyzed, P/Q Mediated, Standard and Over Potentials, Respectively, for the Above Mentioned Reaction. In Homogenous Catalyzed Reaction, the P/Q Mediator and Reactant are in Solution Phase; While for Heterogeneous Catalyzed Reaction, the P/Q is Bounded on the Electrode Surface……………………………………………….

1.2 Structures of (A) Graphite Nanopowder (GNP), (B) Multiwalled Carbon Nanotube (MWCNT) and (C) Graphene Oxide (GO)………………………………

1.3 Schematic Representation of Biosensor Application of Graphene Oxide (GO).

1.4 Structures of (A) MWCNT, (B) SWCNT and Classification of MWCNT Based on their Lattice: Armchair, Zigzag and Chiral…………………………

1.5 Schematic Representation of CNT Applications in Various Fields…………

1.6 Schematic Representations for Efficient Electrocatalysis and Enhanced Redox Properties Influenced by CNT Impurities: (A) Amorphous carbon and (B) Metallic impurities (Fe, Ni, Co and Mo)……………………………………

1.7 Chemical Structures of Polymers: Chitosan, Poly Ionic Liquid and Nafion…

1.8 Schematic Representation for Different Approaches for the Preparation of CNT Based CMEs: (A) Covalent, (B) Non-covalent and (C) Encapsulation...

1.9 Summarizes the Overall Information About the Research Work Done for PhD Thesis Work………………………………………………………………

2.1 Cartoon for Various DNA Modified GCE/GO+Chit Electrode Preparation…. 23

3.1 Cartoon for GNP-PIL Modified Electrode Preparation and its Suitable Ferricyanide Ion-Exchanging Characteristics (A-C). Illustration for Various PIL’s Modified GNP systems for Ion-Exchanging Ferricyanide Ion and their Interaction Behaviour (Controls)……………………………………

4.1 Illustration for In-situ Complexation of Copper Ion with 2,2’-Bipyridine(bpy) Ligand Immobilized Nf-MWCNT Modified Electrode Surface and its Biomimetic Electrochemical Reduction Towards Hydrogen
Peroxide at -0.2V vs Ag/AgCl in Neutral pH. ..........................................................

5.1 Illustration for In-Situ Complexation of a Redox Active Iron Impurity with 2,2’-Bipyridine (bpy) Ligand as Iron(II)tris(2,2’-bipyridine) Complex on MWCNT-*Fe Modified Electrode Surface (A and B) and its Electrochemical Oxidations of DNA’s Purine Bases, Adenine (Electrocatalytic) and Guanine at Discreet Potentials (C). ..............................................................................................................

6.1 Cartoon for the Electrochemical Polymerization of p-SA to Sulfonated Polyaniline (SPAN) (A and B) and Transformation of p-SA to Hydroquinone (C and D) on Iron Impurity Containing MWCNT Modified Glassy Carbon Electrode System by Potential Cycling Experiment Following Set-I or Set-II Conditions Respectively. Followings are Control Experiments Relating to Electrochemical Oxidation/Reduction Reaction of p-SA at the Set-I Condition in pH 7 PBS With; \( \text{N}_2 \) Purged(E), Purified-MWCNT Modified Electrode in Dissolved Oxygen (F) and With \( \text{N}_2 \) Purged Solution and Deliberated added \( \text{H}_2\text{O}_2 \) (500 \( \mu \)M) (G) Conditions. ..............................................................

7.1 Illustration for the Importance of Indole and its Derivatives in Medicinal and Pharmaceutical Chemistry Areas........................................................................

7.2 Cartoon for the Electrochemical Oxidation of Indole to Indole-Tetraone (A-E) on Iron Impurity Containing MWCNT Modified Glassy Carbon Electrode System by Potential Cycling. Followings are the Control Experiments Relating to the Electrochemical Oxidation of Substituted Indole Derivatives (2-Methyl Indole, 3-Carboxaldehyde Indole, 4-Brome Indole; 2F), Isatin (2G), Indene (2H) and Indole at the Condition in pH 7 PBS with \( \text{N}_2 \) Purged and Deliberately Added \( \text{H}_2\text{O}_2 \) (500 \( \mu \)M) (G) Systems. Scheme 2J and 2K Illustrates the Mediated Hydrazine Oxidation and \( \text{H}_2\text{O}_2 \) Reduction Respectively........................................................................................................

7.3 Plausible Mechanistic Pathway for Electrochemical Oxidation Reaction of Indole to Indole-Tetraone Derivative at Iron Impurity Containing MWCNT Modified Electrode Surface in pH 7 PBS...........................................................................
## LIST OF TERMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>µA</td>
<td>Microamphere</td>
</tr>
<tr>
<td>µC</td>
<td>Microcoloumb</td>
</tr>
<tr>
<td>µg</td>
<td>Microgram</td>
</tr>
<tr>
<td>2θ</td>
<td>Delta</td>
</tr>
<tr>
<td>η</td>
<td>Over potential</td>
</tr>
<tr>
<td>ν</td>
<td>Scan rate</td>
</tr>
<tr>
<td>Γ</td>
<td>Surface excess (or) surface coverage</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>Formal or standard potential</td>
</tr>
<tr>
<td>$ΔE_p$</td>
<td>Peak-to-peak separation</td>
</tr>
<tr>
<td>$Δm$; $M$</td>
<td>Delta mass (mass change); Molar mass</td>
</tr>
<tr>
<td>A</td>
<td>Adenine</td>
</tr>
<tr>
<td>A</td>
<td>Area of the electrode</td>
</tr>
<tr>
<td>AA</td>
<td>Ascorbic acid</td>
</tr>
<tr>
<td>Achar; AC</td>
<td>Activated charcoal</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AgCl</td>
<td>Silver Chloride</td>
</tr>
<tr>
<td>Amp $i-t$; Amp $I-T$</td>
<td>Amperometric $i-t$ method</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>BAS</td>
<td>Bioanalytical systems</td>
</tr>
<tr>
<td>bpy</td>
<td>Bipyridine/ bipyridyl</td>
</tr>
<tr>
<td>Bz</td>
<td>Benzene</td>
</tr>
<tr>
<td>C</td>
<td>Cytosine</td>
</tr>
<tr>
<td>CA</td>
<td>Catechol</td>
</tr>
<tr>
<td>Chit</td>
<td>Chitosan</td>
</tr>
<tr>
<td>CME</td>
<td>Chemically modified electrode</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>Cu(bpy)$_2^{2+}$</td>
<td>Copper bipyridyl</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
</tbody>
</table>
CySH : Cysteine
DD water : Double distilled water
D_L : Limit of Detection
DNA : Deoxyribonucleic acid
dsDNA : Double strand deoxyribonucleic acid
Dp : Dopamine
E or E : Electrode potential
E_{app} : Applied potential
ECD : Electrochemical detector
EIS : Electrochemical impedance spectroscopy
E^{o*} : Apparent peak potential
E_{pa} : Anodic peak potential
E_{pc} : Cathodic peak potential
EQCM : Electrochemical quartz crystal microbalance
EtOH : Ethanol
F : Faraday current
Fe(bpy)_3^{2+} : Iron bipyridyl
Fe_2O_3 : Iron (III) oxide
Fe_3O_4 : Iron (II, III) oxide
FIA : Flow injection analysis
f-MWCNT : Functionalized-Multiwalled carbon nanotube
FT-IR : Fourier transform infra red spectroscopy
G : Guanine
GCE : Glassy carbon electrode
GC-Mass : Gas chromatography coupled with mass spectrometry
Glu : Glucose
GMC : Graphitized mesoporous carbon
GNP : Graphite nano powder
GO : Graphene oxide
H_2O_2 : Hydrogen peroxide
HQ : Hydroquinone
Hyd : Hydrazine
Hz : Hertz
i : Current
ipa : Anodic peak current
ipc : Cathodic peak current
IL : Ionic liquid
Ind : Indole
ITO : Indium tin oxide
K₃[Fe(CN)₆] : Potassium hexacyanoferrate (III)
KCl : Potassium chloride
LC-Mass : Liquid chromatography coupled with mass spectrometry
min : Minutes
Mis-DNA : Mismatch DNA
mM : Millimolar
mV : Millivolt
m-SA : Meta-sulfanilic acid
MWCNT : Multi-walled carbon nanotube
n : Number of electrons
nA : Nano amphere
NADH : β-Nicotinamide adenine dinucleotide
Nf : Nafion
nM : Nano molar
NaOH : Sodium hydroxide
NO₂⁻ : Nitrite
NO₃⁻ : Nitrate
o-SA : Ortho-sulfanilic acid
P/Q : Redox mediator
PBS : Phosphate buffer solution
PIL : Poly ionic liquid
p-MWCNT : Purified-multiwalled carbon nanotube
p-SA : Para-sulfanilic acid
Q : Surface charge
Re : Resorcinol
RPM : Rotation per minute
RSD : Relative standard deviation
$R_{sqr}/R^2$ : Regression coefficient
$R_T$ : Retention time
$R_{ct}$ : Conductance resistance
Ru(bpy)$_3^{2+}$ : Ruthenium bipyridyl
S/N : Signal to noise ratio
s : Seconds
SA : Sulfanilic acid
SAM : Self assembled monolayer
SCE : Standard Calomel electrode
SPCE : Screen-printed carbon electrode
SPEAu : Screen-printed gold electrode
SEM : Scanning electron microscopy
ssDNA : Single strand deoxyribonucleic acid
Sty : Styrene
SWCNT : Single walled carbon nanotube
T : Thymine
t : Time
TEM : Transmission electron microscopy
UA : Uric acid
UV-Vis : Ultraviolet visible spectroscopy
$v$ : Scan rate
V : Volt
XRD : X-ray diffraction