

Contents

1	General Introduction	2
1.1	An overview on Metal Hexacyanoferrate (MHCFs).....	2
1.1.1	Crystal structure of Prussian blue	3
1.1.2	Prussian blue Analogues (PBAs).....	5
1.1.3	Synthesis of Prussian blue and its analogues	6
1.1.4	Properties of Prussian blue and its analogues	12
1.1.5	Properties of Mixed metal hexacyanoferrates (MHCFs).....	24
1.2	Prussian blue and its mixed metal analogue in analytical applications ...	27
1.2.1	Electrochemical applications of Prussian blue and its mixed metal analogues.....	28
1.2.2	Artificial Peroxidase like activity of nanomaterial: Special reference to Prussian blue and its analogues in application of H_2O_2	37
1.3	Challenges in Prussian blue and its mixed metal analogues related work... ..	40
1.4	Origin of the present research work	41
1.5	Objective of the present research work	42
1.6	Work plan for the present research work	45
2	THF and H_2O_2 mediated synthesis of nanocrystalline PBNPs and its analytical applications.....	47
2.1	Introduction	47
2.2	Experimental	49
2.2.1	Material and Methods	49
2.2.2	THF and H_2O_2 mediated synthesis of nanocrystalline Prussian blue nanoparticles	49

2.2.3	Measurement and characterization.....	51
2.2.4	Peroxidase like catalytic activity of Prussian blue nanoparticles	52
2.2.5	Preparation of modified graphite paste electrode	53
2.3	Results.....	53
2.3.1	THF and H ₂ O ₂ mediated synthesis of nanocrystalline PBNPs	53
2.3.2	Electrochemical characterization of as synthesized PBNPs	55
2.3.3	Peroxidase like activity of PBNPs made through THF and H ₂ O ₂	55
2.3.4	Electrocatalytic reduction of H ₂ O ₂ on the PBNPs modified electrode	56
2.4	Discussion	64
2.4.1	Optimization of THF and H ₂ O ₂ mediated synthesis of nanocrystalline PBNPs	65
2.4.2	Characterization of THF and H ₂ O ₂ mediated synthesized nanocrystalline PBNPs.....	66
2.4.3	Electrochemical analysis of THF and H ₂ O ₂ mediated synthesized PBNPs	67
2.4.4	Peroxidase like activity of PBNPs	68
2.4.5	Electrocatalytic reduction of hydrogen peroxide over THF, H ₂ O ₂ mediated synthesized PBNPs modified graphite electrode	70
2.5	Stability and Reproducibility	71
3	THF and H ₂ O ₂ mediated synthesis of nanocrystalline Ni-Fe HCFs and its analytical applications	73
3.1	Introduction	73
3.2	Experimental	75
3.2.1	Material and Methods	75

3.2.2	Synthesis of nanocrystalline Ni-Fe hexacyanoferrates (Ni-Fe HCFs).....	75
3.2.3	Structural characterization of Ni-Fe hexacyanoferrates (1:5).....	76
3.2.4	Peroxidase mimetic activity measurement of Ni-Fe HCFs (1:5).....	77
3.2.5	Preparation of modified graphite paste electrode	78
3.2.6	Electrochemical Measurements	78
3.3	Results	79
3.3.1	Synthesis of nanocrystalline Ni-Fe HCFe mediated through $K_3[Fe(CN)_6]$, THF, H_2O_2 and $NiSO_4$	79
3.3.2	Characterization of Ni-Fe HCFs synthesized through THF, H_2O_2 and $NiSO_4$ (1:5).....	81
3.3.3	Peroxidase like activity of Ni-Fe HCFs nanoparticles (1:5).....	84
3.3.4	Electrocatalytic oxidation of hydrazine over Ni-Fe HCFs (1:5) nanoparticles modified electrode	85
3.4	Discussion	93
3.4.1	THF and H_2O_2 mediated synthesis of nanocrystalline Ni-Fe hexacyanoferrates.....	93
3.4.2	Structural analysis of Ni-Fe HCFs nanoparticles (1:5).....	94
3.4.3	Electrochemical analysis of Ni-Fe hexacyanoferrates	96
3.4.4	Peroxidase mimetic behaviour of Ni-Fe hexacyanoferrates (1:5)	96
3.4.5	Electrochemical sensing of hydrazine over Ni-Fe hexacyanoferrates (1:5) modified electrode.....	97
4	Polyethylenimine mediated synthesis of Prussian blue nanoparticles and cooperative self assembly of gold nanoparticles on Polycationic surface	101
4.1	Introduction	101
4.2	Experimental	103

4.2.1	Material and Methods	103
4.2.2	Synthesis of cationic polymer coated nanocrystalline PBNPs and AuNPs assembled PBNPs.....	104
4.2.3	Measurement and characterization.....	105
4.2.4	Electrochemical measurements and preparation of modified graphite paste electrode.....	106
4.2.5	Peroxidase like activity of PBNPs and AuNPs assembled PBNPs.	107
4.3	Results	107
4.3.1	PEI mediated synthesis of nanocrystalline PBNPs and AuNPs assembled PBNPs	107
4.3.2	Structural characterization	108
4.3.3	Electrochemical characterization of PEI mediated synthesized PBNPs	109
4.3.4	Peroxidase mimetic activity of PBNPs and AuNPs assembled PBNPs	109
4.3.5	Electrocatalytic reduction and oxidation of H_2O_2 over PBNPs and AuNPs assembled PBNPs modified electrode.....	110
4.3.6	Magnetic measurement of PBNPs and AuNPs assembled PBNPs.	111
4.4	Discussion	121
4.4.1	PEI mediated synthesis of nanocrystalline PBNPs.....	121
4.4.2	Characterization of cationic polymer coated PBNPs and AuNPs assembled PBNPs	122
4.4.3	Electrochemistry and catalytic activity of PBNPs and AuNPs assembled PBNPs modified electrode	123
4.4.4	Homogeneous catalysis of PBNPs and AuNPs assembled PBNPs	124
4.4.5	PBNPs and AuNPs assembled PBNPs mediated reduction of H_2O_2	125

4.4.6	PBNPs and AuNPs assembled PBNPs mediated oxidation of H_2O_2	126
4.4.7	Magnetic properties of cationic polymer coated PBNPs and AuNPs assembled PBNPs	127
5	PEI mediated synthesis of Cu-Fe HCFs and Ni-Fe HCFs nanoparticles and their analytical applications.....	131
5.1	Introduction	131
5.2	Experimental	133
5.2.1	Material and Methods	133
5.2.2	Synthesis of Cu-Fe hexacyanoferrates and Cu-hexacyanoferrates ..	134
5.2.3	Synthesis of Ni-Fe hexacyanoferrates and Ni-hexacyanoferrates ..	134
5.2.4	Structural characterization of mixed metal hexacyanoferrates	135
5.2.5	Peroxidase mimetic activity of mixed metal hexacyanoferrates.....	135
5.2.6	Fabrication of modified graphite paste electrode.....	136
5.2.7	Electrochemical Measurements	136
5.3	Results	137
5.3.1	PEI mediated synthesis of nanocrystalline mixed metal hexacyanoferrates.....	137
5.3.2	Structural characterization	138
5.3.3	Electrochemical characterization	139
5.3.4	Peroxidase mimetic activity of as synthesized Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5)	140
5.3.5	Electrocatalytic analysis of dopamine, hydrazine and H_2O_2 over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) modified electrode	141
5.4	Discussion	156

5.4.1	PEI mediated synthesis of nanocrystalline Cu-Fe HCF and Ni-Fe HCFs	156
5.4.2	Characterization of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5).....	158
5.4.3	Electrochemical behaviour of mixed metal analogue	160
5.4.4	Peroxidase mimetic activity of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5).....	162
5.4.5	Electrocatalytic oxidation of dopamine, hydrazine and hydrogen peroxide over Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5)	163
5.4.6	Stability and Reproducibility	166
	Summary.....	167
	Future Projection.....	170
	References.....	171
	List of Publication.....	205

List of Figures

- Figure.1.1.** 3D structure of soluble PB (A) and insoluble PB (B), Fe(II) yellow, Fe (III) brown, K magenta, C grey, O red [(Shokouhimehr *et al.* 2010)]. 4
- Figure.1.2.** Cyclic voltammogram of a PB modified electrode showing oxidation and reduction peak [(Ricci and Palleschi 2005)] 14
- Figure.2.1.** Schematic presentation of synthesis of PBNPs from optimum concentration of $K_3[Fe(CN)_6]$, THF and H_2O_2 57
- Figure.2.2.** UV-Vis spectra of systems containing constant concentration of THF (1.2 M) and $K_3[Fe(CN)_6]$ (25 mM) and the varying concentration of H_2O_2 (from 0.003 M to 1.40 M). The corresponding vial visual photographs are shown in the inset of the respective systems. 57
- Figure.2.3.** Systems containing constant concentration of $K_3[Fe(CN)_6]$ (25 mM); and H_2O_2 (0.70 M); and varying concentration of THF (from 0.15 M to 4.5 M). The corresponding vial visual photographs are shown in the inset of the respective systems. 58
- Figure.2.4.** Systems containing constant concentration of THF (1.2 M) and H_2O_2 (0.7 M); and varying concentration of $K_3[Fe(CN)_6]$ (from 3 mM to 45 mM); The corresponding vial visual photographs are shown in the inset of the respective systems. 58
- Figure.2.5.** FT-IR spectra of THF and H_2O_2 mediated synthesized PBNPs..... 59
- Figure.2.6.** XRD pattern of THF and H_2O_2 mediated synthesized PBNPs. 59
- Figure.2.7.** EDS spectra of THF and H_2O_2 mediated synthesized of PBNPs..... 60
- Figure.2.8.** TEM image of THF and H_2O_2 mediated synthesized of PBNPs. 60
- Figure.2.9.** (A) Cyclic voltammograms of THF and H_2O_2 mediated synthesized PBNPs in 0.1 M KNO_3 at various scan rates between $0.01 V s^{-1}$ and $0.3 V s^{-1}$. (B) A typical voltammogram of THF and H_2O_2 mediated synthesized PBNPs at scan rate $0.005 V s^{-1}$. (C) The plots of peak current density vs. scan rate for PBNPs. (D) the plots of peak current density vs. square root of scan rate for PBNPs..... 61
- Figure.2.10.** Colour conversion of o-dianisidine and H_2O_2 in the presence of metal hexacyanoferrates..... 61
- Figure.2.11.** Time dependent absorbance changes at 430 nm in the presence of different concentrations of H_2O_2 (from 0.05 mM to 14 mM and fixed concentration of o-dianisidine (50 μM) catalyzed by PBNPs..... 62
- Figure.2.12.** Kinetic analysis of PBNPs with H_2O_2 as substrate. 62

- Figure.2.13.** Cyclic voltammograms of PBNPs modified electrode in the absence (1) and the presence (2) of 1 mM H_2O_2 in 0.1 M phosphate buffer pH=7.0 containing 0.5 M KCl..... 63
- Figure.2.14.** Amperometric response of PBNPs modified electrode on the addition of varying concentrations of H_2O_2 between 0.01 mM and 5 mM; operating potential, 0.0 V; 0.1 M phosphate buffer (pH=7.0) containing 0.5 M KCl as supporting electrolyte, The inset (B) shows calibration plots for PBNPs..... 63
- Figure.3.1.** Schematic presentation of Ni-Fe hexacyanoferrates formation from THF, H_2O_2 and $K_3[Fe(CN)_6]$ and $NiSO_4$ 86
- Figure.3. 2.** Effect of THF on the formation of Ni-Fe HCF at constant molar ratio of Ni and Fe (1:5) and H_2O_2 86
- Figure.3. 3.** Effect of H_2O_2 on the formation of Ni-Fe HCF at constant molar ratio of Ni and Fe (1:5) and THF..... 87
- Figure.3.4.** AFM image of THF and H_2O_2 mediated synthesized Ni-Fe HCF (1:5). 87
- Figure.3.5.** FT-IR spectra of THF and H_2O_2 mediated synthesized Ni-Fe HCF (1:5). 88
- Figure.3.6.** XRD analysis of THF and H_2O_2 mediated synthesized Ni-Fe HCF (1:5). 88
- Figure.3.7.** SEM image of THF and H_2O_2 mediated synthesized Ni-Fe HCF (1:5). 89
- Figure.3.8.** TEM image of Ni-Fe HCF (1:5), inset shows the respective size distribution. .. 89
- Figure.3.9.** Energy dispersive spectroscopy of THF and H_2O_2 mediated synthesized Ni-Fe HCF (1:5). Inset shows the weight %age of EDS analysis..... 90
- Figure.3.10.** Cyclic voltammetric response of THF and H_2O_2 mediated synthesized Ni-FeHCF modified carbon paste electrodes in 0.1 M KNO_3 at a scan rate of 0.01 $V s^{-1}$ made at different Ni:Fe molar ratio: [A] only PBNPs; [B] Ni- Fe HCF (1:20); [C] Ni-Fe HCF (1:10); [D] Ni-Fe HCF (1:5); [E] Ni-Fe HCF (1:3); [F] Ni-Fe HCF (1:2). 90
- Figure.3.11.** Cyclic voltammetric response of THF and H_2O_2 mediated synthesized Ni-FeHCF modified carbon paste electrodes in 0.1 M KNO_3 at different scan rate of 0.01, 0.02, 0.035, 0.05, 0.07, 0.10, 0.15, 0.20, 0.25, 0.35 $V s^{-1}$ made at different Ni:Fe molar ratio: [A] only PBNPs; [B] Ni- Fe HCF (1:20); [C] Ni-Fe HCF (1:10); [D] Ni-Fe HCF (1:5); [E] Ni-Fe HCF (1:3); [F] Ni-Fe HCF (1:2). 91
- Figure.3.12.** (A) Time dependence absorbance changes at 430 nm in the presence of different concentrations (0.05, 0.10, 0.21, 0.43, 0.86, 1.70, 3.40, 6.80 and 13.60 mM) of H_2O_2 and at fixed concentration of o-dianisidine (50 μM) catalysed by Ni-Fe HCF (1:5), and (B) kinetic analysis of Ni-Fe HCF (1:5) with H_2O_2 as substrate. 91
- Figure.3.13.** Cyclic voltammogram of Ni-Fe HCF (1:5) in the absence (1) and presence (2) of 1 mM hydrazine recorded in 0.1 M $NaNO_3$, pH=7.0 at scan rate of 0.01 $V s^{-1}$ 92

- Figure.3.14.** Amperometric response of Ni-Fe HCF (1:5) modified electrode on the addition of varying concentration of hydrazine between 0.01 M to 5 mM; operating potential 0.3 V; 0.1 M NaNO₃ was the supporting electrolyte..... 92
- Figure.3.15.** Calibration curve for hydrazine analysis..... 93
- Figure.4.1.** UV-Vis spectra of showing requirement of optimum concentration of both K₃[Fe(CN)₆] and PEI in acidic medium for the synthesis of PBNPs. 112
- Figure.4.2.** UV-Vis spectra of system containing constant concentration of K₃[Fe(CN)₆] (25 mM) and the varying concentration of PEI (A) 10 mg/ml (B) 20 mg/ml (C) 30 mg/ml and (D) 40 mg/ml. 112
- Figure.4.3.** UV-Vis spectra of system containing constant concentration of PEI (20 mg/ml) and the varying concentrations of K₃[Fe(CN)₆] (A) 10 mM (B) 25 mM (C) 35 mM and (D) 50 mM respectively..... 113
- Figure.4.4.** Schematic presentation of cationic polymer coating and formation of PBNPs (A), AuNPs (B) and AuNPs assembled on cationic surface of PBNPs (C)..... 113
- Figure.4.5.** XRD pattern of PBNPs (A) and AuNPs assembled PBNPs (B). 114
- Figure.4.6.** TEM image of PBNPs (A) and AuNPs assembled PBNPs (B). Inset to the figure shows selected area electron diffraction pattern. 114
- Figure.4.7.** Cyclic voltammograms of PBNPs (A) and AuNPs assembled PBNPs (B) electrode in 0.1 M KNO₃ at the scan rate of: 10, 20, 35, 50, 70, 100, 150, 200, 250, and 300 mV s⁻¹ consecutively..... 115
- Figure.4.8.** The plot of anodic and cathodic current density vs. scan rate (A and C) and square root of scan rate (B and D) for PBNPs (A and C) and AuNPs assembled PBNPs (B and D) respectively. 115
- Figure.4.9.** Time dependent absorbance changes at 430 nm in the presence of different concentrations of H₂O₂ (from 0.18 mM to 25 mM) and fixed concentration of o-dianisidine (50 μM) catalyzed by PBNPs (A) and Kinetic analysis of PBNPs (B)..... 116
- Figure.4.10.** Time dependent absorbance changes at 430 nm in the presence of different concentrations of H₂O₂ (from 0.18 mM to 25 mM) and fixed concentration of o-dianisidine (50 μM) catalyzed by AuNPs assembled PBNPs (A), and Kinetic analysis of AuNPs assembled PBNPs (B). 116
- Figure.4.11.** Cyclic voltammograms of PBNPs (A) and AuNPs assembled PBNPs (B) in absence (1) and the presence (2) of 1 mM H₂O₂ at the scan rate of 0.01 V s⁻¹ in 0.1 M phosphate buffer (pH=7.0) containing 0.5 M KCl..... 117
- Figure.4.12.** Amperometric response of PBNPs (1) and AuNPs assembled PBNPs (2) modified electrodes at 0.2 V vs. Ag|AgCl on the addition of varying concentrations of H₂O₂ in 0.1 phosphate buffer containing 0.5 M KCl..... 117
- Figure.4.13.** Calibration curve of H₂O₂ reduction obtained from amperograms of PBNPs (1) and AuNPs assembled PBNPs (2)..... 118

- Figure.4.14.** Chronoamperograms for PBNPs (A) and AuNPs assembled PBNPs (B) modified electrode in the absence (black curve) and in the presence (red curve) of 1 mM H_2O_2 . The step potential was -0.05 V vs. Ag|AgCl. Inset: corresponding plots of I_{cat}/I_L vs. $t^{1/2}$ in 0.1 M phosphate buffer containing 0.5 M KCl as supporting electrolyte..... 118
- Figure.4.15.** Cyclic voltammograms of PBNPs (A) and AuNPs assemble PBNPs (B) in absence (1) and presence (2) of 1 mM H_2O_2 at the scan rate of $0.01 V s^{-1}$ in 0.1 M phosphate buffer (pH=7.0) containing 0.5 M KCl..... 119
- Figure.4.16.** Amperometric response of PBNPs (1) and AuNPs-PBNPs (2) modified electrodes at 0.6 V vs. Ag|AgCl on the addition of varying concentrations of H_2O_2 in 0.1 phosphate buffer (pH=7.0) containing 0.5 M KCl..... 119
- Figure.4. 17.** Calibration curve of oxidation of H_2O_2 obtained from amperograms of PBNPs (1) and AuNPs assembled PBNPs (2)..... 120
- Figure.4.18.** Normalized zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of PBNPs at different applied field (H): A=25, B=50 and C=100 Oe; (D) Magnetization hysteresis loops at 2 K, 5 K, and 10 K respectively (D). 120
- Figure.4.19.** Normalized zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of PBNPs (A) and AuNPs assembled PBNPs (B) at 100 Oe applied field (H). .. 121
- Figure.5.1.** Schematic presentation of PEI mediated synthesis of Cu-Fe hexacyanoferrates and Ni-Fe hexacyanoferrates nanoparticles. 143
- Figure.5. 2.** UV-Vis spectroscopy of Cu-Fe HCFs (1:1) and Ni-Fe HCFs (1:5) made through $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ at 60 °C in 3 hours. 143
- Figure.5. 3.** Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) (B) Ni-Fe HCFs (1:5) [made through $K_4Fe(CN)_6$ and PEI at 60 °C]; and (C) Cu-Fe HCFs (1:1) (D) Ni-Fe HCFs (1:5) [made through $K_3Fe(CN)_6$ and PEI at 60 °C]..... 144
- Figure.5. 4.** UV-Vis spectroscopy of (A) Cu-Fe HCFs (1:1) (B) Ni-Fe HCFs (1:5) made at (1) room temperature (2) 90 °C and (3) 60 °C. 144
- Figure.5. 5.** Cyclic voltammetry of (A) to (C) for Cu-Fe HCFs (1:1) and (D) to (F) for Ni-Fe HCFs (1:5) [synthesized at room temperature, 60 °C and 90 °C] in 0.1 M KNO_3 as electrolyte..... 145
- Figure.5. 6.** Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5) made without PEI at scan rate of $0.01 V s^{-1}$ in 0.1 M KNO_3 as a electrolyte; UV-Vis spectroscopy (C) of the (1) Ni-Fe HCFs (1:5) and (2) Cu-Fe HCFs (1:1) synthesized without PEI in 24 hours..... 145
- Figure.5. 7.** FT-IR spectra of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5)..... 146
- Figure.5. 8.** XRD analysis of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5)..... 146
- Figure.5. 9.** TEM image of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5); inset to the each figure shows the SAED pattern of respective metal hexacyanoferrates; SEM image of (C) Cu-Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5). 147

- Figure.5. 10.** EDS spectra of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5). 147
- Figure.5. 11.** Cyclic voltammetry response of Cu-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at scan rate of 0.01 V s^{-1} made at different Cu:Fe molar ratio [A] PBNPs; [B] Cu:Fe (1:10); [C] Cu:Fe (1:5); [D] Cu:Fe (1:3); [E] Cu:Fe (1:2); [F] Cu:Fe (1:1); [G] Cu:Fe (2:1); [H] Cu:Fe (3:1); and [I] CuHCFs 148
- Figure.5. 12.** Cyclic voltammetry response of Cu-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at scan rate of 0.01, 0.02, 0.035, 0.05, 0.07, 0.10, 0.15, 0.20, 0.25, 0.30 V s^{-1} made at different Cu:Fe molar ratio [A] PBNPs; [B] Cu:Fe (1:10); [C] Cu:Fe (1:5); [D] Cu:Fe (1:3); [E] Cu:Fe (1:2); [F] Cu:Fe (1:1); [G] Cu:Fe (2:1); [H] Cu:Fe (3:1) and [I] CuHCFs..... 149
- Figure.5. 13.** The plots of peak current density vs. scan rate for Cu-Fe HCFs made at different molar ratio of Cu:Fe [A] 1:10 [B] 1:5 [C] 1:3 and [D] 1:2..... 150
- Figure.5. 14.** Cyclic voltammetry response of Ni-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at scan rate of 0.01 V s^{-1} made at different Ni:Fe molar ratio [A] only PBNPs; [B] Ni:Fe (1:20); [C] Ni:Fe (1:10); [D] Ni:Fe (1:5); [E] Ni:Fe (1:3); [F] Ni:Fe (1:2); [G] NiHCFs. 150
- Figure.5. 15.** Cyclic voltammetry response of Ni-Fe HCFs modified graphite paste electrode in 0.1 M KNO_3 at varying scan rate of 0.01, 0.02, 0.035, 0.05, 0.07, 0.10, 0.15, 0.20, 0.25, 0.30 V s^{-1} made at different Ni:Fe molar ratio [A] PBNPs; [B] Ni:Fe (1:20); [C] Ni:Fe (1:10); [D] Ni:Fe (1:5); [E] Ni:Fe (1:3); [F] Ni:Fe (1:2); and [G] NiHCFs. 151
- Figure.5. 16.** The plots of peak current density vs. scan rate for Ni-Fe HCFs made at different molar ratio of Ni:Fe [A] PB [B] 1:20 [C] 1:20 [D] 1:10 [E] 1:5, [F] 1:3 and [G] 1:2. 151
- Figure.5. 17.** Cyclic voltammetry of (A) to (C) for Cu-Fe HCFs (1:1) and (D) to (F) for Ni-Fe HCFs (1:5) under different pH=4.0 (phthalate buffer), pH=7.0 (phosphate buffer) and pH=9.0 (borate buffer) containing 0.5 M KCl..... 152
- Figure.5. 18.** Time dependent absorbance changes at 430 nm in the presence of different concentration (25, 18, 13, 6.5, 3.25, 1.5, 0.75, 0.37 and 0.18 mM) of H_2O_2 and fixed concentration of o-dianisidine (50 μM) catalyzed by (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5); and kinetic analysis of (C) Cu:Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5) with H_2O_2 as substrate. 152
- Figure.5. 19.** Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5) in the absence (1) and presence of (2) 2 mM and (3) 5 mM dopamine recorded in 0.1 M phosphate buffer containing 0.5 M KCl, (pH=7.0) at scan rate of 0.01 V s^{-1} ; (B) amperometric response of (C) Cu-Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5) modified graphite paste electrode on the addition of varying concentration of dopamine between 0.01 μM to 5 mM; operating potential 0.2 V; 0.1 M phosphate buffer containing 0.5 M KCl was the supporting electrolyte; the inset (C') and (D') shown the calibration curve for dopamine analysis for the respective modified electrode. 153
- Figure.5. 20.** Cyclic voltammogram of (A) Ni-Fe HCFs (1:5) (B) Cu-Fe HCFs (1:1) in the absence (1) and presence of (2) 1 mM and (3) 5 mM hydrazine recorded in 0.1M NaNO_3 scan rate of 0.01 V s^{-1} ; (B) amperometric response of (C) Ni-Fe HCFs

(1:5) and (D) Cu-Fe HCFs (1:1) modified graphite paste electrode on the addition of varying concentration of hydrazine between 0.01 μM to 5 mM; operating potential 0.3 V; 0.1 M NaNO_3 was the supporting electrolyte; the inset (C') and (D') shown the calibration curve for hydrazine analysis for the respective modified electrode..... 154

Figure.5. 21. Cyclic voltammogram of (A) Cu-Fe HCFs (1:1) and (B) Ni-Fe HCFs (1:5) in the absence (1) and presence of (2) 1 mM H_2O_2 recorded in 0.1 M phosphate buffer containing 0.5 M KCl, pH=7.0 at scan rate of 0.01 V s^{-1} ; (B) amperometric response of (C) Cu-Fe HCFs (1:1) and (D) Ni-Fe HCFs (1:5) modified graphite paste electrode on the addition of varying concentrations of H_2O_2 between 0.01 μM to 5 mM; operating potential 0.0 V; 0.1 M phosphate buffer containing 0.5 M KCl was the supporting electrolyte; the inset (C') and (D') shown the calibration curve for H_2O_2 analysis for the respective modified electrode..... 155

List of Table

Table.1.1. Electrochromic colour changes in different MHCs.	19
Table.1.2. Curie temperature (T _c) of Prussian blue analogues.	20
Table.2.1. Characteristics of PBNPs sol as a function of H ₂ O ₂ concentration.	50
Table.2. 2. Characteristics of PBNPs sol as a function of THF concentration.....	50
Table.2.3. Characteristics of PBNPs sol as a function of K ₃ [Fe(CN) ₆] concentration.	51
Table.3.1. Synthesis of Ni-Fe HCF as a function of variable composition of K ₃ [Fe(CN) ₆] and NiSO ₄	76
Table.4.1. Characteristics of PBNPs as a function of PEI concentration.....	104
Table.4.2. Characteristics of PBNPs as a function of K ₃ [Fe(CN) ₆] concentration.	105

List of Scheme

Scheme.1. 1. Examples of oxidase catalyzed reactions.	42
Scheme.1. 2. Reactions involved in GOD/POD system during pathological detection of blood glucose.	43
Scheme.2.1. Scheme for THF and H ₂ O ₂ mediated synthesis of PBNPs.	64
Scheme.2.2. Schematic presentation of colorimetric detection of H ₂ O ₂ using PBNPs catalyzed colour reaction.	69
Scheme.3.1. Schematic presentation for the synthesis of Prussian blue and Ni-Fe hexacyanoferrates.....	81

LIST OF SYMBOLS AND ABBREVIATIONS

PB	Prussian blue
PBNPs	Prussian blue nanoparticles
PW	Prussian white
PBAs	Prussian blue analogues
MHCF	Metal hexacyanoferrate
FeHCF	Iron hexacyanoferrate
NiHCF	Nickel hexacyanoferrate
Ni-Fe HCF	Nickel-Iron hexacyanoferrate
Cu-Fe HCF	Copper- Iron hexacyanoferrate
3-APTMS	3-aminopropyltrimethoxysilane
H ₂ O ₂	Hydrogen peroxide
Hz	Hydrazine
Do	Dopamine
HAuCl ₄	Tetrachloroaurate
THF-HP	Tetrahydrofuran-hydroperoxide
THF	Tetrahydrofuran
PEI	Polyethylenimine
GOx	Glucose oxidase
AuNPs	Gold nanoparticles
HRP	Horseradish peroxidase
CV	Cyclic voltammetry
GPE	Graphite paste electrode
CPE	Carbon paste electrode
K _m	Michaelis-Menton constant
V _{max}	Maximal reaction velocity
λ _{max}	Absorbance maxima